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THE SYSTEM, CU–FE–S.

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INTRODUCTION.

PURSUANCE of the problem of synthesizing the sulphides of copper and iron has led to determinations of dissociation pressures of the binary compounds CuS and FeS_2 by heating under

controlled pressure of sulphur vapor.[1] Attempts thus to synthesize the ternary compounds made it evident that a systematic study was required of the ternary system Cu-Fe-S, involving only solid phases and vapor.[2] The plan and results may be stated briefly. Thus, if granular mixtures of the two binary compounds lowest in sulphur, Cu_2S and FeS, are heated in sulphur vapor almost to melting so that they gradually take up sulphur, the following changes take place: (1) each kind of grain absorbs sulphur and becomes a sulphur-rich solid solution, Cu_2S_{1+} and FeS_{1+}; (2) adjacent grains interchange iron and copper, forming copper-rich and iron-rich ternary solid solutions; (3) these solid solutions, in proper proportions, react to produce an intermediate compound which, itself, forms extensive solid solutions; (4) finally, with falling temperature and increasing pressure these solid solutions break down progressively into more definite compounds richer in sulphur, until the final product is a mixture of CuS and FeS_2.

The temperature range has been about 400° to 950° C., and the pressure range, 2 to 760 mm. At a particular pressure, a rise of temperature to the points at which melting begins, sets the lower limits to the amount of sulphur that the solids can hold, and thus limits the field of study. A lowering of the temperature to the points at which condensation to liquid sulphur begins fixes the upper limits of sulphur content. Between these limits at known copper-to-iron ratios, by control of temperature and pressure, composition and phase equilibria are established, which are then determined in the cooled products by microscopical and chemical analyses. The details for particular sets of conditions can be presented satisfactorily only by means of diagrams which become a part of the discussion.

[1] Allen, E. T., and Lombard, R. H.: Am. J. Sci., vol. 43, p. 175, 1917. For other methods see the above, and Juza, R., and Biltz, W.: Z. anorg. allgem. Chem., vol. 205, p. 273, 1932.

[2] Preliminary outlines were presented in the Report of the Director of the Geophysical Laboratory, Carnegie Institution of Washington Year Book No. 25, pp. 62–69, 1925–6; and No. 30, pp. 82–84, 1931–2.

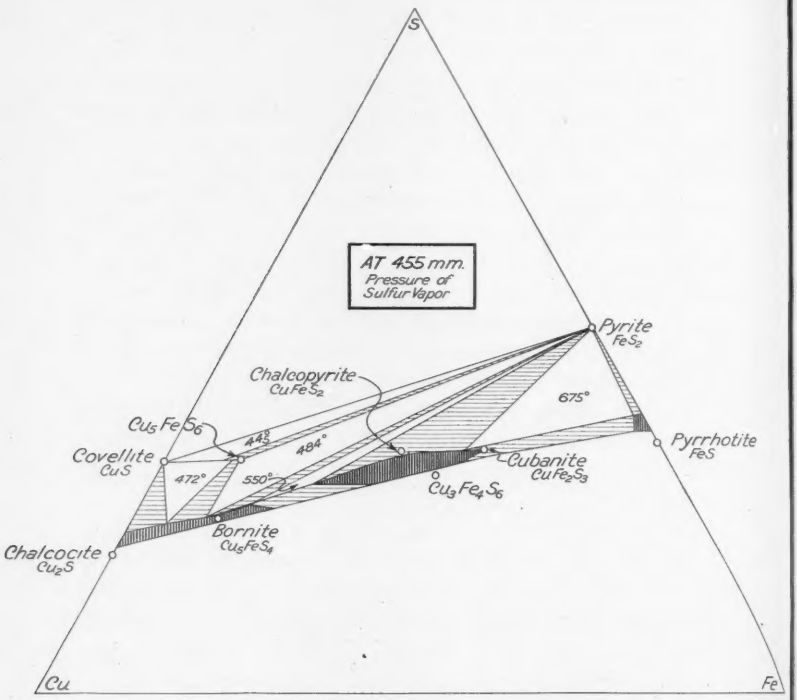

FIG. 1. Types of fields.—This composition triangle in weight per cent. shows the 4 binary and 5 ternary crystalline compounds of Cu, Fe and S. All but two have mineral names. These and their solid solutions or inversion forms are stable with sulphur vapor at a pressure of 455 mm., either alone or in presence of each other without liquid, as shown in Fig. 1. A different set of *three* is stable at each of the five single temperatures indicated within the clear triangular areas. Each of the three has a definite composition represented by a corner of the triangle, within which any proportions of the three may be present. Most of the corners are points on the boundaries of solid solutions.

Where a solid solution, as *one* phase, covers an area, heavy vertical lining is used. The large central field is the intermediate solid solution, and the others are chalcocite solid solution and pyrrhotite solid solution. The sulphur content decreases with rising temperature, but before enough

The compounds (Fig. 1) are described in Table I. Most of them are well-known minerals; $Cu_5Fe_4S_6$ is new; and probably Cu_5FeS_6 has been observed in ores with bornite.[3]

MATERIALS AND METHODS.

Owing to the difficulty of obtaining the necessary quantities of natural copper-iron sulphide minerals of sufficient purity, most of the work was done with artificially prepared copper-iron *mattes,* which were made at any desired Cu-Fe ratio, usually by fusing together at 1100–1200° C., in an atmosphere of H_2S, a mixture of metallic copper and Merck's "Iron Sulphide, Reagent, Granulated." The finely chipped Cu and the 80-meshed iron sulphide, intimately mixed in the desired proportions, were contained in a cylindrical Acheson graphite crucible[4] of 15 mm. inside diameter, 2.5 mm. wall thickness, 11 cm. height, and fitted with a graphite cap. During its heating in a vertical, platinum-wound electric furnace, the crucible was contained at the bottom of a glazed porcelain tube, 2.5 cm. internal diameter; wall thickness, 3 mm.; and length, 50 cm. Hydrogen sulphide gas was led directly into the crucible through a porcelain tube which fitted into a hole in the crucible cover; two other smaller holes in the cover provided exit for the gas. The temperature of the matte was determined approximately by a Pt–Pt 10 per cent. Rh thermo-element, enclosed in a Marquardt porcelain protecting tube that

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sulphur is expelled to bring the sulphur content down to the join between Cu_2S and FeS, melting begins (Fig. 2).

The other fields (lightly lined, horizontally) lie between solid solutions, or between compounds and solid solutions, and *two* crystalline phases appear in each field.

In the upper part of Fig. 1, liquid sulphur containing very little CuS and FeS_2 in solution is in equilibrium with covellite and pyrite at 411+°; and in the lower part liquids and crystals are present as mentioned under Fig. 2. Also see under Fig. 2 for other pressures.

[3] Murdock, Joseph: Microscopical determination of the opaque minerals. John Wiley and Sons, New York, 1916, pp. 64–5.

[4] Silica glass can be used if the sulphide melt contains no oxide.

rested on the crucible cover. The temperature inside the crucible at various depths was 20–35° higher than that indicated by the thermoelement on the cover. The main object in measuring the temperature was to make sure that the fusion temperature had been reached. The porcelain tube containing the graphite crucible was closed with a graphite cap through which projected the H_2S tube and the thermoelement tube. Sulphur collected in the cooler parts of the porcelain tube.

About two hours were required to heat the mixture to 1100–1200°, after which it was kept at this temperature for about ten minutes and then cooled in the hydrogen sulphide. Mixtures of copper with iron sulphide heated only once as above do not react fully with the hydrogen sulphide, but—depending upon the Cu-Fe ratio—may contain besides the sulphide the following: a lump of metallic copper in the bottom of the crucible; a thin metallic shell, mostly iron, surrounding the lump of sulphide; finely divided iron and copper throughout the matte. The lump of sulphide was then powdered and, together with the metallic portions, remelted. After 3 to 5 such meltings the matte usually had a maximal sulphur content, and when cold contained no disturbing amounts of coarse metallic constituents.

The matte was next ground to pass a 100-mesh per inch sieve and analyzed. Frequently, due to spattering from crucible or to undetermined causes, the Cu-Fe ratio was not sufficiently close to that intended. In such cases the calculated amount of copper or copper sulphide or of iron sulphide was added and the matte twice remelted in H_2S, and the analysis repeated.

The copper used in preparing the mattes was of the grade used at the Geophysical Laboratory for calibrating thermoelements at the melting point of copper.[5] The Merck "Iron Sulphide" contained 67 to 70 per cent. Fe and 0.4 per cent. of substance insoluble in hot HCl or HNO_3. Microscopic examination indicated that this was siliceous. Polished surfaces of this iron sulphide showed also a little metallic iron, and in scattered patches a grayish white constituent minutely intergrown with the sulphide.

[5] Allen, E. T.: Am. J. Sci., vol. 29, p. 159, 1910.

In the first and second melts made during the preparation of mattes rich in iron, traces of the grayish-white constituent were often detected, but in subsequent melts were not seen. Loebe and Becker [6] noticed such a structure when Fe and FeS were melted and cooled with access to air. They refer to it as the "Fe-S-O" eutectic. The Merck iron sulphide doubtless contained much iron oxide (Table 5, end).

Natural bornite, chalcopyrite, cubanite, and pyrite were used somewhat, but usually merely to establish the identity of their behavior with that of the synthetic products. In the accompanying tables these are designated by name or formula. The phases and analyses of products derived from them fall in line with those from mattes.

The *apparatus* used by us for studying equilibrium was adapted for one operator from the type used by Allen and Lombard [7] for determining the dissociation pressures of pyrite and covellite (Table 10*A*), these determinations being preliminary to the present study. Briefly, it was an evacuated glass tube [8] with a cylindrical bulb at each end, one bulb containing sulphur and the other several 0.5-gram samples of mattes in the form of 100-mesh powder, each sample contained in a small length of open tube. The bulb tube was heated in a horizontal, electric, tube furnace divided vertically and sliding open so that the matte bulb could be kept at the temperature at which equilibrium was being studied, while the sulphur bulb could be kept at the temperature that corresponds to the vapor pressure of sulphur under which it was desired to heat the matte. The temperature of the bulbs was measured by calibrated thermoelements, and the pressure-temperature relations for sulphur were determined from the known

[6] Z. anorg. Chem., vol. 77, p. 301 and fig. 16, 1912.

[7] Allen, E. T., and Lombard, R. H.: Am. J. Sci., 4th ser., vol. 43, pp. 175–195, 1917.

[8] Pyrex glass tubes are preferable to the Jena Combustion glass tubes used at first because they crack less frequently when the cold tube is introduced into the hot furnace. However, above 635° C. evacuated Pyrex tubes collapsed, and so above this temperature glazed Vitreosil (fused silica) was used.

vapor pressure curve of sulphur,[9] in the way described by Allen and Lombard.[1] The tubes were heated first about 6 hours. If the matte had reacted by absorbing much sulphur the product usually was caked fairly hard. If so, it was pulverized before being heated for another 6 hours. Often a third heating was made. When the heating was completed the furnace enclosing the sulphide bulb was quickly slipped off, the sulphur bulb withdrawn from its furnace, and the sulphide bulb cooled in a blast of air. The rates of cooling of the charge and the sulphur usually maintained a sufficiently close balance of pressure to prevent disturbing changes of sulphur content of the charges during cooling. Three exceptions when pressures were highest (450–760 mm.) may be noted. (1) In a run at 725° at 455 mm. a delay of several seconds in withdrawing the sulphur bulb was accompanied by the following higher analytical values for sulphur at the Cu-Fe ratios indicated: 5 : 1, 0.2 per cent.; 3 : 1, 0.4 per cent.; 1 : 2, 0.25 per cent.; 1 : 5, 0.45 per cent. (2) A few of the higher sulphur percentages at 750°–950° may have come about by such absorption. (3) A very rapid reaction involving phase changes, but not much change in sulphur content, is described under Table 41.

In a series of comparable experiments, inconsistencies in *analytical* results may be attributed to three chief causes. (1) The analytical error in sulphur (by difference) probably seldom exceeds 0.2 per cent. (2) Absorption or evolution of sulphur during cooling—as above considered. (3) Lack of equilibrium at the temperature of heating. In many instances approach toward sulphur equilibrium was made from both directions. In the tables the differences in sulphur percentages at stated ratios of Cu to Fe may be slightly misleading when different mattes are compared because the actual ratios are not quite as indicated by the rounded numbers. Such analyses must be plotted.

During cooling, phase changes such as inversions and unmixings took place which had to be considered in relation to the

[9] For recalculations based on recent measurements see Table 10*A*.

textures present at the onset of cooling. The powdered charges were prepared for microscopical examination as follows.

Near one end of a glass slip a small drop of a selected sealing wax was flowed, upon this a little heap of the sulphide powder was placed and slumped down by gentle heating, then a bit of cover glass was used to give a flat surface. When cold the cover glass was sprung off and the grains ground on hard cardboard with tin oxide (putty powder) or rouge. A final polish with tin oxide or rouge on chamois was often made. Considerable differences of color, partly due to rapid tarnish, were produced by different methods of polishing.

Following is the method used for the quantitative determination of copper and iron in the products.[10] Chips of glass were always present in the samples from evacuated tubes.

Treat 0.4 gram of the powder in a porcelain casserole, with 25 cc. 1 : 1 HNO_3 and evaporate nearly to dryness on a steam bath. The casserole is covered at first to avoid spattering. Add 8 cc. 1 : 1 HNO_3 and 20 cc. H_2O, filter off the residue containing sulphur and traces of Cu, Fe and insoluble matter. Ignite the residue in a porcelain crucible; evaporate it to dryness with 1 cc. 1 : 1 HCl and then with 1 cc. HNO_3, take up with a few drops of dil. HNO_3 to dissolve Cu and Fe, and filter. Ignite the residue and weigh as acid insoluble matter. Add the filtrate to that above containing most of the Cu and Fe. Determine the copper in this solution electrolytically. Evaporate to dryness the solution remaining after electrolysis, which contains the Fe and a trace of Cu. Moisten with conc. HCl, evaporated to dryness to convert to chlorides, take up the residue with dil. HCl, precipitate the trace of Cu in the solution with H_2S, filter, ignite the precipitate, and weigh as CuO. Evaporate the filtrate containing the Fe to dryness, moisten with 1 : 1 HNO_3, and evaporate to dryness to oxidize the iron. Treat the residue with 1 : 1 HNO_3, and determine the Fe gravimetrically as Fe_2O_3 by double precipitation with SiO_2-free NH_4OH.

The compositions given in the tables are analytical.

[10] This method was suggested by E. T. Allen and had been used previously in this Laboratory in studies of the copper-iron sulphides.

PHASE RELATIONSHIPS IN MATTES MELTED UNDER THEIR OWN DISSOCIATION PRESSURES.

Considerable solid solution has been indicated by previous work [11] for fused mixtures of Cu_2S and FeS. We have studied also mixtures of the more sulphur-rich solid solutions $Cu_2S_{1.04}$ and $FeS_{1.08}$.

One-gram mixtures in various proportions, as shown in Tables 2 to 4, were melted in small graphite crucibles [2] enclosed in evacuated Vitreosil tubes of about 8 cc. volume. The temperature was held at about 1230° for ten minutes and then at about 1170° for 50 minutes. The tubes were cooled out of the furnace. During cooling fine-grained structures due to unmixing and inversions developed, and from the more sulphur-rich melts about .0020 g. of sulphur deposited on the walls of the tubes.

The microscopic textures of the products might be expected to reflect the general characters of the published fusion diagrams, made on the assumption that Cu_2S-FeS melts behave like a binary system. Although two eutectoid textures were observed (Tables 2 and 3), grains of FeS-solid solution were found in a 3.5 : 1 preparation containing about 20 per cent. by weight more copper than the previous indefinite limit (*ca.* 1 : 1) would indicate. To account for the discrepancy would require other methods of study. It may be said, however, that in our melts the irregular distribution of the pyrrhotite in roundish grains does not suggest unmixing. The pyrrhotite is a solid solution containing here, according to microscopical estimation, about 5 per cent. of copper. (See Table 2, 1 : 10.) In melts somewhat richer in sulphur (Table 4) a ternary compound appears at intermediate Cu : Fe

[11] The equilibrium diagram of the system Cu_2S-FeS, by Clark B. Carpenter and Carle R. Hayward, Engineering and Mining Journal-Press, vol. 115, p. 1,055, 1923, is introduced by a summary of work previous to 1910. Versuche zur Feststellung der Verwandtschaftsreihe der Metalle gegenuber Schwefel nach der "mikrostatischen" Method, von W. Guertler, Metall und Erz, vol. 22, p. 199, 1925. Sur la composition des mattes de cuivre, par B. Bogitch, C. R., vol. 182, p. 468, 1926. Über die Ursache der Haarkupferbildung im Kupferstein, von P. P. Fedotieff (Experimentelle Teil von D. N. Nedrigaloff). Z. anorg. Chem., vol. 167, p. 329, 1927. See papers and references by W. Guertler and O. Reuleaux, Metall und Erz, vol. 24, pp. 97, 99, 129, 1927, and by D. D. Howat, J. Roy. Tech. Coll., vol. 3, p. 587, 1936.

ratios, but textural features indicate that it develops in part at least in these particular mattes as a result of unmixing of the chalcocite solid solution. Metallic copper results from unmixing.

Fused Mixtures of Cu_2S and FeS.

Preparation and Properties of Cu_2S and FeS.—Two different 10-gram samples of Cu_2S were prepared by melting two synthetic chalcocites of the composition $Cu_2S_{1.042}$ and $Cu_2S_{1.112}$ with the weight of copper calculated to give $Cu_2S_{1.000}$ and $Cu_2S_{0.9982}$, respectively.

Cu_2S does not hold copper in solid solution at room temperature, and dissolves very little just above its melting point. Thus, the $Cu_2S_{0.9982}$ matte (79.89 per cent. Cu, 20.11 per cent. S) contained by analysis 0.04 per cent. excess of copper over Cu_2S, and careful microscopical examination showed a minute trace of metallic copper in it. The absence of such solid solution was confirmed during the preparation of a chalcocite by melting copper in hydrogen sulphide. The first melt consisted of a small button of copper, overlain with a thick layer of chalcocite which contained fine, evenly distributed, megascopically visible metallic copper. The chalcocite layer contained 80.07 per cent. Cu, or 0.25 per cent. excess copper over Cu_2S. Microscopical estimation of the metallic copper gave 0.19 per cent. by volume or 0.32 per cent. by weight. Therefore, the excess copper was present as metallic copper. Some of the metallic copper formed moss-like growths from surfaces of the chalcocite after solidification; and much of it formed evenly distributed small globules or rounded masses. Evidently a little liquid copper separated from the melt during the solidification of the sulphide.

Two 10-gram samples of FeS were made by melting in evacuated tubes the pyrrhotites $FeS_{1.045}$ and $FeS_{1.028}$, mixed with a weight of Kahlbaum's iron powder calculated to give $FeS_{1.000}$. Their compositions were $FeS_{1.002}$ and $FeS_{0.9982}$ respectively. From the first, an extremely small, very magnetic portion was separated in which metallic iron was detected microscopically in amount estimated to be less than 0.01 per cent. of the whole sample. No

metallic iron was noted in the second, but probably it was present because this sample contained more magnetic grains than the first. Also, after melting the $FeS_{1.002}$ in vacuo with metallic iron so as to give a 64 per cent. iron content, the amount of the strongly magnetic portion, and of the metallic iron had increased appreciably. Thus no solid solution of iron in FeS was found.

The location of preparations with respect to Cu to Fe molal ratio will be referred to as 9 : 1, 4 : 1, etc.

Compositions from Cu_2S to 4 : 1. Discussion of Table 2.— In the products ranging from Cu_2S to 4 : 1 there are present (1) a sulphide portion, which under low magnifications [12] varies progressively in color from the grayish white of Cu_2S to a grayish yellow-orange similar to the mineral bornite; and (2) metallic copper, as a mossy covering of late formation; and to a less extent, as tiny globular or irregular masses in the interior of, or among, the sulphide grains, which probably formed while the melt solidified.

The sulphide portion is (at high temperature) a single phase, a chalcocite solid solution.

Compositions from 3.5 : 1 to FeS. Two solid phases appear in the products, the orange-colored *chalcocite solid solution* and a light yellow, harder phase which is a *pyrrhotite solid solution.* The latter increases with the iron content of the charge up to a composition between 6.55 and 2 per cent. (5 per cent. estimated) of copper where it becomes the sole phase.

Traces of metallic *iron* were seen in all these products. Metallic *copper* appeared on exposed surfaces of the orange grains.

Fused Mixtures of $Cu_2S_{1.016}$ and $FeS_{1.036}$. (Table 3.)

$Cu_2S_{1.016}$ and $FeS_{1.036}$ were prepared by melting together in small evacuated tubes the proper mixtures of $Cu_2S_{1.042}$ and copper, and of $FeS_{1.082}$ and iron. The compositions and descriptions of the solidified melts appear in Table 3.

[12] The minute secondary structures seen under high magnifications lose identity under these conditions. They are described in some detail under the heading of unmixing. They have been considered in relation to equilibrium at high temperatures.

The intermediate compositions lie about 0.2 per cent. below a straight line joining $Cu_2S_{1.016}$ and $FeS_{1.036}$, Fig. 1. They contain approximately 0.3 to 0.8 per cent. more sulphur than those on the line Cu_2S-FeS.

From Cu_2S to 5:1 the sulphide portion (chalcocite solid solution) is gray to grayish-yellow-orange and usually has the mottled structure previously mentioned.[12]

From 4:1 to $FeS_{1.036}$ the chalcocite solid solution decreases progressively and the pyrrhotite solid solution increases.

The principal effect of increasing the sulphur content has been to lessen the amounts of the metallic phases present during solidification, and unmixed during cooling. As before, these occur in maximum amount at about 4:1 or 5:1 and decrease as the amount of the chalcocite solid solution decreases. Metallic iron was observed, in very small amounts only in the narrow range 3.5:1 to 3:1. In the Cu_2S-FeS series it occurred over a much wider range.

Fused Mixtures of $Cu_2S_{1.042}$ and $FeS_{1.082}$. (*Table 4.*)

The $Cu_2S_{1.042}$ was one of several synthetic chalcocites prepared from metallic copper by several heatings and meltings in hydrogen sulphide until the copper had reacted completely. The $FeS_{1.082}$ was one of several synthetic pyrrhotites prepared by repeatedly melting Merck's iron sulphide in hydrogen sulphide.

The fact to be noted in these data is the appearance, near the middle of the series, of a new solid solution with an end member near $Cu_3Fe_4S_6$ which was not present in corresponding products of lower sulphur content. It is softer and darker yellow than the pyrrhotites, and will be referred to as the intermediate solid solution.

PROPERTIES OF COPPER-IRON MATTES PREPARED BY MELTING IN HYDROGEN SULPHIDE.

From Fig. 2 it is evident that in approaching equilibrium compositions from the low-sulphur side, the starting materials must be lower in sulphur than the melting boundary. Mattes prepared

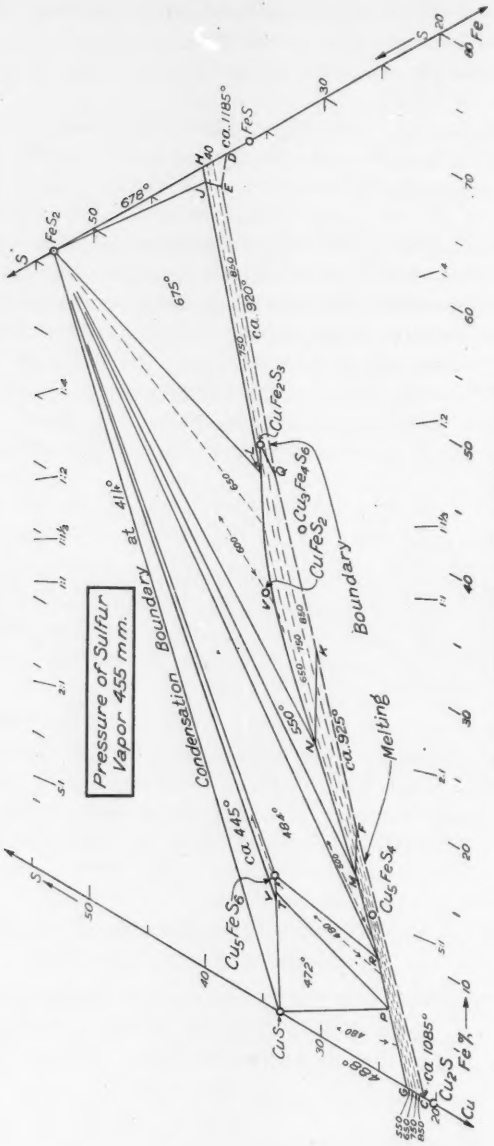

FIG. 2. (Explanation on opposite page.)

FIG. 2. Isotherms.—Fig. 2 is the middle part of Fig. 1 with added details. Isotherms that are field boundaries are necessarily at irregular intervals, some have been indicated at irregular intervals by arrows, and others have been drawn complete at regular intervals. In all fields having two solid phases (see Figs. 1 and 4) the compositions of the two phases which are stable together are on the same isotherm at opposite boundaries of the field. In fields having only one solid phase the isotherms must be determined entirely by experiment.

To obtain the pressure (455 mm.) indicated on the diagrams, sulphur was heated at 411°, but because of the slight solubility of CuS and FeS_2 in liquid sulphur a slightly higher temperature (411+°) is required for the equilibrium here. This straight isotherm is the condensation boundary. Upon it is superposed the 445° isothermal boundary from which, up to the temperatures at which the sulphides begin to melt, sulphur diminishes. The eutectic between Q and E is near 920°, and between F and K near 925°. Out from these eutectics the series of solid solutions melt progressively up to about 950°, 1085° and 1185°. The compositions to which these temperatures apply form the melting boundary. Between these two boundaries the figure is a diagram of a single complex surface consisting of triangular levels and warped or vertical slopes. Two other boundaries complete the enclosure of the surface. They may be called systemic boundaries, for they follow parts of the boundaries of the system Cu-Fe-S. Each is a broken line along which the equilibrium surface intersects the vertical plane of two of the components S-Fe and S-Cu (see Fig. 4). Each consists of three segments: (1) a vertical segment representing the stability range of temperature for the compound with most sulphur; (2) a horizontal segment at the dissociation temperature of this compound; (3) an inclined curved segment for stable compositions of solid solutions of the compound with least sulphur.

From the melting boundary, the three fields of solid solutions, and the two fields connecting them, descend steeply to the boundaries at which reactions with sulphur take place. (Clearly shown in Fig. 4.)

The pyrrhotite H is in equilibrium with FeS_2 at 678°. The pyrrhotite solid solution J combines with sulphur at 675° to form FeS_2 and a cubanite solid solution with composition L. The series of solid solutions L-V-N are stable successively with FeS_2 from 675° to 550°. But at 550° N combines with sulphur to produce FeS_2 and chalcocite solid solution M. The series of solid solutions M-R are stable successively with FeS_2 from 550° to about 484°, at which R and FeS_2 combine with sulphur to form the compound Cu_2FeS_4, from which solid solutions extend to T (and Y). As temperature falls, successive members of this series and of the series R-P are in equilibrium together. At 472° P combines

(Continued on next page.)

in hydrogen sulphide, as in Table 5, are suitably fine grained and contain less sulphur than the indicated melting boundary—nearly ½ per cent. less near Cu_2S, and about 1½ per cent. less near $Cu_3Fe_4S_6$ and FeS.

Small cubo-octahedrons on Matte No. 9—about 8:1—show the form of the high-temperature chalcocite. (See discussion, Table 8.)

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with sulphur forming CuS and T. The chalcocites P-G are stable with CuS from 472° to 488°. The solid solutions Cu_5FeS_6-Y and FeS_2 are in equilibrium from 484° to 44$_5$°, likewise in a vertical field the solid solutions T-Y and CuS from 472° to about 445° at which Y combines with sulphur to form CuS and FeS_2. These two occupy a vertical field from about 445° to 411+°.

Beginning with each of the eutectics, rise of temperature to *complete melting* of the several solid solutions, expels sulphur and thus carries the compositions slightly beyond the melting boundary—probably not to exceed 0.5 per cent.

The general effect of *increasing pressure* is to first elevate the surface represented by the diagram, without much changing its shape. However, the condensation boundary rises faster than the lowest isothermal field so that at a few atmospheres a fixed (quintuple) point in the system is to be expected at which sulphur vapor and liquid, and three solids (CuS, FeS_2, $Cu_{5+}FeS_{6+}$) are in equilibrium. At higher pressures $Cu_{5+}FeS_{6+}$ would not then be stable.

At *lower pressures* the surface descends, apparently without much change of shape. Between the melting boundary and the Cu-Fe boundary a complex series of reactions takes place at temperatures above the beginning of melting when pressures are very low.

Construction points (see also Tables 17*A* and 36*A*) for Fig. 2, in the order Cu Fe S:

C 79.1 —— 20.9; D —— 61.4 38.6; E 2.2 58.8 39.0; F 56.4 16.7 26.9; G 77.5 —— 22.5; H —— 59.5 40.5; J 1.2 58.5 40.3; K 41.2 28.3 30.5; L 25.4 39.2 35.4; M 59.6 13.4 27.0; N 48.2 21.3 30.5; P 70.9 5.0 24.1; Q 26.1 39.7 34.2; R 66.8 8.2 25.0; T 57.5 8.6 33.9; V 34.9 30.7 34.4; Y 57.5+ 8.6 — 33.9; Y′ 57.5 ± 8.6 ∓ 33.9.

The decimal figures for points M and N and those along the melting boundary are probably significant but not accurate; for the other points these figures are probably nearly accurate.

At the Cu-Fe ratio of 1 : 1 ⅓ the matte, No. 31, consisted entirely of the new soft yellow phase mentioned in the preceding section. Here it has the composition $Cu_3Fe_4S_6$ which later experiments show is at or near a corner of an area of extensive solid solution extending toward chalcopyrite, cubanite, and chalcocite. This phase will be called the intermediate solid solution. $Cu_3Fe_4S_6$, compared directly with chalcopyrite in polished section, is distinctly duller, darker and slightly orange in color. In hardness it is not decidedly different from chalcopyrite, and it is probably rhombohedral (Table 8).

The phases present between 1 : 1 ⅓ ($Cu_3Fe_4S_6$) and $FeS_{1.07}$ are the soft yellow one (intermediate solid solution) and pyrrhotite. The proportion of the intermediate solid solution decreases as Cu-Fe decreases, until between 3.5 and 2.0 per cent. Cu the matte is a homogeneous pyrrhotite. The fresh powder, in bulk, of a pyrrhotite solid solution (Matte No. 47) containing only 1 per cent. of copper is distinctly yellower than one with the same sulphur content without copper, No. 49. In a mixture of the two powders, mounted and polished, the two kinds of grains are indistinguishable.

Lumps of matte consisting largely of pyrrhotite solid solution are crumbly, owing (probably) to a low-temperature inversion. (See " Phase Changes . . . During Cooling.")

Decomposition of $Cu_3Fe_4S_6$ by Loss of Sulphur.

The cooled 1 : 1 ⅓ matte, No. 33, which had been melted in hydrogen sulphide at 1250°, was not homogeneous soft yellow, as it was after melting at 1170°, but contained small quantities of pyrrhotite and chalcocite solid solutions. Also the 1 : 2 matte, No. 35, heated at 1250°, contained chalcocite solid solution which was not present after heating at 1170°. The sulphur content of each of these mattes is slightly less than of those at 1170°. Also, the mattes made from $Cu_2S_{1.042}$ and $FeS_{1.082}$, Table 4, which have relatively even less sulpur, contain correspondingly smaller amounts of the soft yellow phase and greater amounts of the

other phases. Finally, with still less sulphur, on the line $Cu_2S_{1.016}$-$FeS_{1.036}$, the soft yellow phase has disappeared completely.

Low-Sulphur Mattes.

In *Table 6* are given the compositions and phases of three mattes at various stages of sulphur absorption starting with iron sulphide and metallic copper.

The compositions of some of the melts given are as much as 3 per cent. below the line Cu_2S-FeS. They differ from melts on the line only in having greater amounts of metallic iron and copper, and in first melts a little of the iron oxide which was present in the original iron sulphide.

The form in which the metal occurs in the first melt in the preparation of a matte in hydrogen sulphide differs for different Cu-Fe ratios. From Cu_2S to about 4 : 1 part of the excess metal, just before solidification begins, is a copper button in the bottom of the crucible. From 2 : 1 to about 1 : 4 metallic iron may solidify on the cooler walls of the crucible, and form a thin metallic shell around portions of the lump. The metallic copper in such mattes is mostly distributed throughout the lump as though it separated along with the crystalline constituents. Between 1 : 4 and pyrrhotite the metallic shell is small or absent in the first melt, and the metal present is distributed throughout the lump.

COPPER-IRON SULPHIDES HEATED AS POWDERS AT 900° IN SULPHUR VAPOR AT PRESSURES OF 2, 58, AND 455 MM.

At 900° equilibrium was satisfactorily approached from both directions in 12-hour heatings at 58 mm. (Table 10), but at 2 mm. 12 hours appeared too short (Table 9), and at 455 mm. removal of the tubes from the furnaces was not accomplished quickly enough (Table 16). The 900° isotherm at 58 mm. has phases similar to, and almost coincides ($\pm$ ½ per cent. S) with the "Melting Boundary" as drawn for 455 mm. (Fig. 2). Also, it represents slightly higher sulphur than the mattes at

1170° above described (½ per cent. at the chalcocite end, and 1 per cent. at the pyrrhotite end).

THE STABILITY OF $CuFeS_2$ (CHALCOPYRITE), $CuFe_2S_3$ (CUBANITE), Cu_5FeS_4 (BORNITE), AND Cu_5FeS_6 IN SULPHUR VAPOR.

The mineral names, chalcopyrite, cubanite and bornite, are used, although inversions or slight changes in composition during heating may occur.

Heatings were made in the double furnace of Allen and Lombard,[1] chemical analyses showed at what temperatures and pressures sulphur was absorbed or evolved, and microscopical examinations indicated phase changes. Many details appear under other headings.

Chalcopyrite.

Many preliminary heatings of five different chalcopyrites were made at temperatures of 375° to 525° and pressures of sulphur vapor of 1 to 50 mm., but only at temperatures above 500° and pressures above 40 mm. did the results indicate systematic changes. It became evident that the reaction of chalcopyrite involving the absorption of sulphur lagged greatly at the lower temperatures and pressures because pyrite, one of the reaction products, was slow to crystallize. Once started, the reaction sometimes became complete in 6 hours. On the other hand, loss of sulphur began without apparent lag.

After sufficient heating within the range 10 mm. to 610 mm. and 525° to 625° samples analyzing as $CuFeS_2$ contained a little pyrite, but otherwise resembled chalcopyrite, whereas samples 0.5 per cent. by weight lower in sulphur than this formula were homogeneous. Thus, in this range chalcopyrite of the theoretical composition is not quite stable, but a dissociation pressure curve for $CuFeS_{1.95}$ (Cu 34.9, Fe 30.7, S 34.4, per cent. by weight, *V* of Fig. 2) was obtained. See Table II and Fig. 3. The data presented later for the high temperature ternary relationships show that this composition is on the boundary of a series of solid

solutions which invert, probably to the chalcopyrite structure (Tables 21–27).

Cubanite.

Because of the slight changes of composition over large intervals of temperature and pressure, only at three widely separated pressures was a stability temperature determined. Natural cubanite, containing a little pyrrhotite, and 1 : 2 matte were used. The results show that cubanite can be prepared in sulphur vapor under the three following conditions: 804°, 760 mm.;

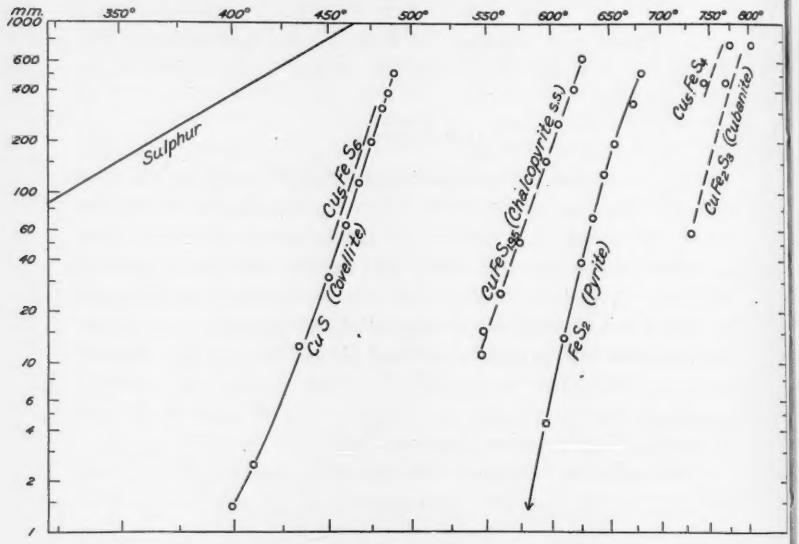

FIG. 3. Vapor pressure of sulphur, and dissociation pressures of sulphides of iron and copper; temperature in ° C. and pressure in millimeters of Hg are read off directly; mm. written for $\log_{10} p$ mm., and ° C. written for $\frac{1}{° C. + 273.1}$. Sulphur, from West and Menzies; covellite and pyrite, from Allen and Lombard. With respect to the slopes of curves, pyrite has about the same relation to selenium that covellite has to sulphur.

766°, 455 mm.; 736°, 58 mm. By using a plot for vapor pressures, such as Fig. 3, intermediate conditions can be found. For details see Table 12.

Bornite.

Temperature changes at 455 mm. and 760 mm. affect the composition of bornite so little that it is not difficult to prepare an apparently homogeneous material of the composition Cu_5FeS_4 by the methods already described. The relation of its crystal structure to that of bornite is not definitely known (discussion Tables 13 and 14). An approximate dissociation curve from the results in Table 13 is shown in Fig. 3. At these temperatures of formation, this Cu_5FeS_4 is a chalcocite solid solution stable at 775°, 760 mm., and at 740°, 455 mm. (See the ternary diagrams.)

Cu_5FeS_6.

The data in Tables 32–35 and 37–42 indicate dissociation pressures for Cu_5FeS_6 slightly above those for covellite.

PHASE (SOLIDS + VAPOR) RELATIONSHIPS IN THE SYSTEM Cu-Fe-S AT 455 MM. (0.60 ATM.) PRESSURE OF SULPHUR VAPOR.

Within the limits of error of the experimental work, and therefore in the accompanying discussion, the partial pressure of sulphur vapor may be considered the total pressure. At temperatures above 1200° copper and iron in any proportions in sulphur vapor at 455 mm. (0.60 atm.) form liquid sulphides. Progressive cooling causes the separation of three series of solid solutions with eutectics for which temperatures are not known. On an ordinary ternary composition diagram the continuous line of compositions along which liquid sulphide disappears (or melting begins) is the *melting boundary* of the area of the diagram in which the phases are solids and vapor. Such phases persist through a long interval of cooling until sulphur vapor begins to condense and introduce a liquid phase. The line of compositions along which liquid sulphur thus begins to appear is the

condensation boundary. Inasmuch as CuS and FeS_2, which are stable at this boundary, are but little soluble in liquid sulphur, the temperature along this line is practically that of sulphur boiling at 455 mm.

The materials heated were: (1) purified minerals; (2) mattes as described in Tables 5 to 8; (3) mattes which had been given a heating in sulphur vapor or hydrogen sulphide whereby they contained, before the final heating, more sulphur than the equilibrium products.

The mattes often contained two or three sulphides and a few per cent. of metallic copper and iron. Their reactions to form equilibrium products involved a redistribution of copper and iron as well as sulphur throughout each grain and amongst adjacent grains. At temperatures above 680° the chief phases in the mattes differed but slightly from those in the equilibrium products which, furthermore, were all solid solutions with variable sulphur content—a condition favorable to the rapid diffusion of sulphur, for which 6-hour heatings seem to have been sufficiently long. The proper copper-iron ratio and attendant phase equilibrium were sometimes not attained in 6 hours. At lower temperatures, at which changes of phase were accompanied by large changes in sulphur content, 18-hour heatings were sometimes too short for complete reaction.

Types of Fields in the Ternary System Cu-Fe-S, for Pressure of Sulphur Vapor 455 mm., the Phases being Vapor and Solids.

(See Figs. 1, 2, and 4.)

Types of Fields.

1. The field contains only one solid phase (field of solid solution). Shapes of the isotherms subject to experimental determination. Examples, chalcocite solid solution (G-C-F-M-R-P).
2. The field contains two solid phases.
   A. The fields slope.

a. Both solid phases are solid solutions. In such fields isotherms are straight lines connecting the two solid solution boundaries at points of equal temperature. The isotherms may be sub-parallel, divergent, or crossed. Example, the field between chalcocite solid solution and the intermediate solid solution (M-N-F-K).

b. One solid solution and one definite compound. The isotherms diverge as straight lines from the compound to points on the boundary of the solid solution. Example, the field between the intermediate solid solution and pyrite (FeS_2-L-N).

B. The fields are vertical, and therefore the isotherms on the triangular diagram are superposed, and on the three-dimensional surface are parallel.

a. Both solid phases may be binary solid solutions with respect to each other (no example).

b. Both solid phases may be definite compounds (CuS and FeS_2).

c. One solid phase is a definite compound, the other a solid solution (CuS and $Cu_{5+}FeS_{6+}$).

3. The field contains three solid phases. The phases, each of definite composition, may be present in any proportion, reacting with vapor at a single temperature. If A, B, and C represent the solid phases the reactions may be:

$$A + \text{sulphur} \rightleftharpoons B + C \qquad (1)$$
$$A - \text{sulphur} \rightleftharpoons B + C \qquad (2)$$

Examples, (1) the field between the chalcocite solid solution P and covellite and the solid solution T (P-CuS-T); and (2) the field between the chalcocite solid solution R and pyrite and the compound Cu_5FeS_6 (R-FeS_2-Cu_5FeS_6). The reactions are:

$$P + \text{sulphur} \rightleftharpoons CuS + T \qquad (1)$$
$$Cu_5FeS_6 - \text{sulphur} \rightleftharpoons R + FeS_2 \qquad (2)$$

Description of the Fields.

Order of Description.—The diagrams, Figs. 1 and 2, are a part of this presentation. The original data are contained in tables, several of which may refer to one field. The discussions of the tables often contain details not tabulated, but which materially supplement the descriptions that here follow. The diagrams are so largely determined by fields of solid solution that these fields will be considered first, then the intervening fields, and finally the rest of the fields in about the order of decreasing temperature.

Field of chalcocite solid solution, C-F-M-R-P-G.—Chalcocite solid solutions are stable at the melting boundary, C-F, where temperatures are not known accurately, but they probably fall gradually from about 1085° at C, to about 925° a eutectic temperature, at F. With lowering pressures the melting boundary migrates toward less sulphur, to near the line of compositions Cu_2S-FeS, where temperatures are higher (Table 45).

Within the field, temperatures fall rapidly from those of the melting boundary to 472° as sulphur increases. The isotherms nearly parallel the long directions of the field, as slightly curved lines (Tables 15 to 34). At the boundary F-M the intermediate solid solution is stable with the chalcocite solid solution, and from M to G the following series of phases resulting from reactions with sulphur are stable with the chalcocite: pyrite, $Cu_{5+}FeS_{6+}$, and covellite. The compositions of iron-free chalcocites with excess sulphur, C-G, are given in Table 14.

Well within this field is the composition Cu_5FeS_4 of the mineral bornite.

Area of Intermediate Solid Solution, V-N-K-Q-$CuFe_2S_3$-L.—At 455 mm. this large area probably is a single field (but see discussion of Tables 19–21), and the solid phase rhombohedral in crystallization (Table 8). The crystal structure is probably that of the compound $Cu_3Fe_4S_6$, although solid solution is required to stabilize it here. Extensive solid solution carries compositions nearly half-way to Cu_2S and CuS, nearly to $CuFeS_2$, and—as here interpreted—quite to $CuFe_2S_3$. The nearly straight

but undetermined line K-Q is the melting boundary. Q-$CuFe_2S_3$-L are the compositions stable in contact with pyrrhotites (Tables 16 to 19), and L-V-N are those stable in contact with pyrite (Tables 20 to 27, especially Table 24). Compositions along N-K and the corresponding ones of the chalcocite solid solutions along M-F are stable together. (See Table 28.) Isotherms have been traced within the field at temperatures 850° to 550° (Tables 16 to 27).

Field of Pyrrhotite Solid Solutions, H-J-E-D.—At this pressure, as with chalcocites, only the sulphur-rich half of the known pyrrhotites are within the field, and variations of sulphur or copper of only one or two per cent. are represented. Melting is near 1185° at D (Table 45), but is probably decidedly lower at E. Compositions E-J are stable at progressively lower temperatures in contact with corresponding intermediate solid solutions Q-$CuFe_2S_3$-L. Along H-J pyrite and pyrrhotites are stable together. The most sulphur-rich pyrrhotite here has the composition $FeS_{1.19}$ (Tables 15 and 20). The isotherms across this field are so short that they show no change of direction at the boundary E-J.

Field between Chalcocite Solid Solution and Intermediate Solid Solution, F-K-N-M.—At each temperature between about 925° and 550° a particular pair of these solid solutions is stable. Each of the pair may be any fraction of the whole, therefore isotherms are straight lines. The 925° isotherm is a boundary of the field because along it eutectic melting introduces a new phase; similarly 550°, because the reaction, N + sulphur $\rightleftharpoons$ M + pyrite, introduces a new phase. (See Table 28.)

Field between Pyrrhotite Solid Solution and Intermediate Solid Solution, E-J-L-$CuFe_2S_3$-Q.—Like the preceding field, the melting boundary is near 920°, and the reaction boundary near 675°. The compound $CuFe_2S_3$ (cubanite) is on the boundary of the intermediate solid solution at 766°. Evidently over a considerable range at higher and lower temperatures it maintains a type of crystal structure (see Table 24), although sulphur and iron lost at higher temperatures, and iron lost at lower tempera-

tures, are replaced by copper. These losses furnish the iron for the pyrrhotites required to establish the equilibrium at the temperatures concerned.

Field between Pyrrhotite and Pyrite, J-FeS_2-H.—According to Tables 8 and 10*A* the equilibrium $FeS_2 \rightleftharpoons FeS_{1.18} + S$ is at 678°, 455 mm. The little copper — maximum *ca.* 1 per cent.— replacing iron in the pyrrhotite must make a little change in the equilibrium temperature, but the 3° indicated on the diagrams may be more than 3° in error. In theory, straight isotherms radiate from FeS_2 to points on H-J. (See Tables 20 and 21.)

Isothermal Field of Intermediate Solid Solution, Pyrrhotite Solid Solution, and Pyrite, J-L-FeS_2.—When, through decreasing temperature, pyrrhotite saturated with copper becomes saturated with sulphur also, a further decrease of temperature causes the pyrrhotite to break down into pyrite and a member of the intermediate solid solution, according to the reaction: Pyrrhotite s. s. (J) + Sulphur $\rightleftharpoons$ Pyrite + Intermediate s. s. (L). The temperature of the reaction is fixed, but the three solid phases may be present in any proportions. (See Tables 20 and 21.)

Field between Pyrite and the Intermediate Solid Solution, FeS_2-L-V-N.—Pyrite and a long series of intermediate solid solutions (Tables 20 and 21) are stable together here over a temperature interval of more than 100°. Isotherms 675° to 550° are straight lines radiating from FeS_2 to the points on the boundary of the solid solution which are in equilibrium with FeS_2. At such a point, V, on the 620° isotherm the solid solution has nearly the theoretical composition of chalcopyrite (Table 11). These solid solutions that contain more copper than does chalcopyrite usually unmix and invert while cooling, and then show a minutely reticulate structure of orange and yellow, or streaks of orange in yellow.

Isothermal Field Containing Pyrite, Intermediate Solid Solution, and Chalcocite Solid Solution, FeS_2-N-M.—The intermediate solid solution that is saturated with copper and sulphur at 550° has the composition N. This composition is, at this temperature, in equilibrium with pyrite and the chalcocite solid

solution M. Thus, N + Sulphur ⇌ M + Pyrite. (See Tables 27 and 28 for details.)

Field between Chalcocite Solid Solution and Pyrite, M-R-FeS_2.—As temperatures fall from 550° to 484° pyrite remains the solid phase stable with chalcocite solid solution, moreover the extent of solid solution decreases markedly, from M to R. Isotherms radiate as straight lines from FeS_2 to points on M-R.

Isothermal Field Containing Chalcocite Solid Solution, Cu_5FeS_6, and Pyrite, R-Cu_5FeS_6-FeS_2.—At 484° a chalcocite solid containing about one half the maximum amount of iron (composition R) reacts with a little pyrite and several per cent. of sulphur to form the new ternary compounds Cu_5FeS_6. Reaction velocities here are so slow, even when this temperature is overstepped a few degrees in either direction, that equilibrium has been approached rather than reached in the experiments defining this field (Tables 32 and 33, 6:1 to 2:1). *The new compound, Cu_5FeS_6,* shows, on polished surfaces between crossed polarizers, strong selective bireflection with colors from brass-yellow to dull copper. In ordinary light the color of most sections is scarcely different from that of bornite or the corresponding chalcocite solid solution. It is soft like bornite. Its preparation requires careful control of temperature and pressure. Between 450° and 500° its dissociation pressure curve almost coincides with that of covellite (Fig. 3). At a given pressure pyrite is a stable decomposition product at either slightly higher or lower temperatures. The time required for preparation is much less if the original material is a 5:1 matte than if it is a mixture of covellite and pyrite. Some grains in sections of bornite ores called by Murdock[3] "unknown mineral" and in some cases "orange bornite" have bireflection and hardness similar to $Cu_{5+x}FeS_{6+x}$.

Field between Chalcocite Solid Solution and Cu_5FeS_6 Solid Solution, R-P-T-Cu_5FeS_6.—Each composition along R-P has a corresponding composition along Cu_5FeS_6-T, stable with it at a temperature between 484° and 472°. Straight isotherms join sets of points on the two boundaries of solid solution (Tables 32 to 34a, 11:1 to 6:1).

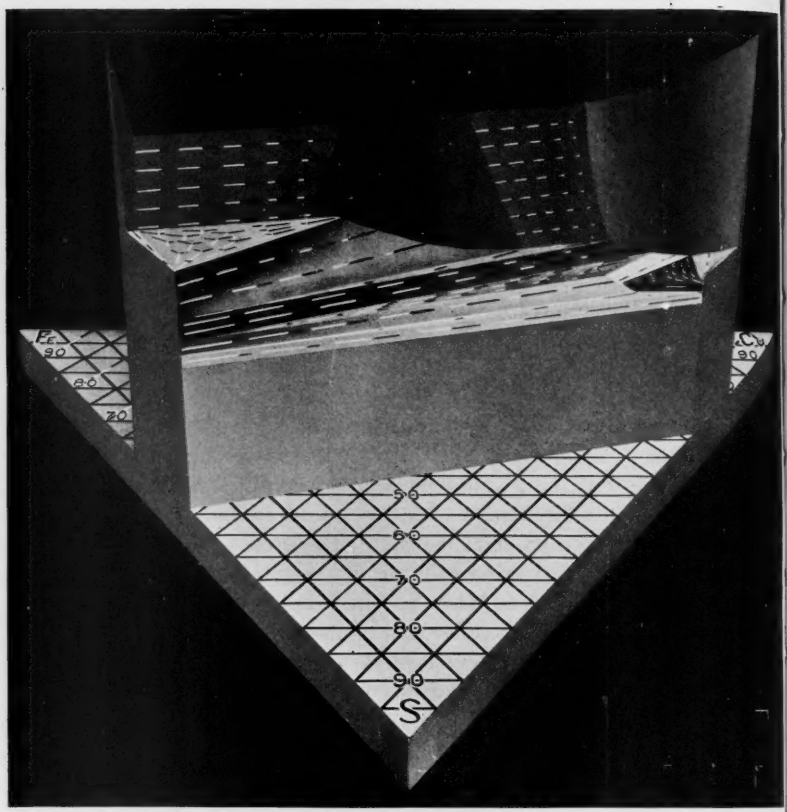

FIG. 4. Three-dimensional surface.—From the fields and isotherms of Figs. 1 and 2 the spacial diagram, Fig. 4, was constructed. The diagram itself consists of only the steps and rises, while the sides and front serve merely to support the surface the proper distance, representing temperature, above the composition triangle. Isotherms are not drawn on the surface, but in all the fields in which two crystalline phases are present, segmented horizontal lines, which are isothermal, have been drawn indicating approximately by differences in color the relative proportions of the two phases that are in equilibrium. In the isothermal fields the sets of three radiating lines indicate the proportions of the phases present at each center.

Reactions and other details are outlined in the legend of Fig. 2.

Isothermal Field Containing Chalcocite Solid Solution, Cu_5FeS_6 Solid Solution, and Covellite, P-T-CuS.—At 472° chalcocite solid solution combines with sulphur to form covellite and $Cu_{5+}FeS_{6+}$. This field has the characteristics of the field J-FeS_2-L In ordinary light polished sections of preparations within this field show great color contrasts: covellite is light blue to dark blue, $Cu_{5+}FeS_{6+}$ is yellow to copper-colored, and chalcocite solid solution is dark neutral gray.

Field between Chalcocite Solid Solution and Covellite, P-G-CuS.—Covellite is in equilibrium here with a series of chalcocites over the temperature range 488°–472°. Isotherms radiate from covellite to points on the solid solution boundary P-G. Color of the chalcocites varies from bluish gray at G to a darker neutral gray at P (Tables 32 to 34a, ∞ : 1 to 11 : 1).

Field between Pyrite and the Cu_5FeS_6 Solid Solutions, FeS_2-Cu_5FeS_6-T-Y-Y′.—As Cu_5FeS_6 dissolves CuS the stability temperatures of this phase and pyrite drop from 484° to about 445°. The composition, Y′, for the lowest temperature is not known, but for this temperature or for some intermediate temperature the maximum content of CuS, Y, probably [13] is greater than at T. This composition determines the extent of the field as shown on a plane triangle. On the solid model, Fig. 4, the line Y-FeS_2 might be on an overhanging bulge. (See Tables 32–36, 6 : 1, to 2 : 1.)

Isothermal Field Containing Pyrite and $Cu_{5+}FeS_{6+}$ and Covellite, FeS_2-Y-CuS.—At 44_5° the reaction is Y + sulphur ⇌ Pyrite + covellite (see Table 36).

Field between Covellite and $Cu_{5+}FeS_{6+}$, CuS-Cu_5FeS_6.—In Fig. 2 this field is represented by a line, but the three-dimensional surface of Fig. 4 shows it as a vertical plane through CuS and Cu_5FeS_6. In this plane run the isotherms 472° to 44_5°, which continue to FeS_2.

Field between Covellite and Pyrite, CuS-FeS_2.—As in the preceding field the isotherms 44_5° to 411+° are in a vertical plane. Here the plane passes through CuS and FeS_2.

[13] The data of Tables 34, 40 and 41 strongly indicate that solid solution is increasing at T.

COORDINATES OF ISOTHERMS.

Within fields of solid solution isotherms are curved, but in Fig. 2 all the other segments of isotherms between the condensation and the melting boundaries are straight lines. All of these isotherms, except those above the lowest melting boundary, traverse the whole diagram. Some of those at regular intervals have been traced directly, some have been interpolated. Tables 17*A* and 36*A* give the coordinates from which the isotherms of the diagram were constructed.

The isotherms that continue from a corner of each isothermal field (except *ca.* 445°) are mostly not shown but may be described as follows: 675° runs from L subparallel to 650 across the diagram to the line C-G; 550° runs from M as shown; 484° runs from R to between P and G, thence to CuS; 472° runs from T to FeS_2.

The isothermal boundaries 678° from FeS_2 to H, and 488° from CuS to G represent points on the pyrite and covellite dissociation pressure curves, respectively. From H and G they continue across the diagram. If the isotherms F-K and Q-E are in the right order the 920° isotherm crosses the diagram within the fields of solid phases, but the 925° isotherm passes into fields containing liquid, between Q and K (near Q). The isotherms 920°–1185° in the pyrrhotite field pass into liquid fields, likewise 925°–1085° in the chalcocite field, and also those above 920° in the field of intermediate solid solution.

The condensation boundary is a straight isotherm connecting CuS and FeS_2. In the vertical plane above it are the isotherms between 411+° and *ca.* 445°. According to the diagram the isotherms covering the interval *ca.* 445° to 472° leave CuS as horizontal lines in a vertical plane, run to the boundary T-Y, thence to FeS_2.

TYPES OF FIELD BOUNDARIES.

The boundaries between the fields of the isobaric surface of Fig. 4 concern directly only solid phases, but around the fields as a whole the boundary concerns also gas and different types of

liquids. A part of this boundary follows binary boundaries of the ternary system (systemic boundaries). Five of the fields are horizontal, triangular, three phase fields, on all sides of which are two phase fields. Two of the fields are vertical and variously bounded, and eleven are sloping.

A. Peripheral boundaries
  1. Melting boundaries between
    a. Liquid sulphide and a variable solid solution (D-E).
    b. Liquid sulphide and two invariable solid solutions (E-Q).
  2. Condensation boundary between
    a. Liquid sulphur and two sulphides (CuS-FeS_2 at 411+°).
  3. Systemic boundaries between sulphur vapor and:
    a. A compound (vertical at FeS_2 between 411+° and 445°).
    b. Two solids of unique composition (FeS_2-H).
    c. A variable solid solution (D-H).

B. Interfield boundaries between two fields with the following number of solid phases:
  1. One and two (E-J).
  2. Two and two (Cu_5FeS_6-T).
  3. Two and three (J-L).

HEATINGS AT VARIOUS TEMPERATURES, AND PRESSURES OTHER THAN 455 MM.

In Tables 9 to 15 some data at temperatures above 600° have been presented. In the tables now to be considered and 41*A* some of the heatings were among the first made, and were of an exploratory nature. The background of the work at 455 mm. pressure is used in presenting these other details, in fact, the compositions along the field boundaries at all pressures between 58 mm. and 760 mm. are so near those at 455 mm. that a more detailed study than has been made would be required to show

any differences. Between the higher and lower pressures the temperatures along the boundaries are most different at high temperatures. A summary of such differences is given in Table 41, discussion.

At 760 mm.

The more detailed work at temperatures below 550° is given in Tables 37 to 41, with a discussion following Table 41. The 480° isotherm at 760 mm. practically coincides with the 475° isotherm at 455 mm., likewise the 540° with the 520° isotherm, and the 800° with the 765° isotherm.

At 300 mm.

From Table 42 it is evident that for temperatures 400° to 500° the reactions that take place at 455 mm. take place also at 300 mm., at temperatures about 10° less than at 455 mm.

At 58 mm.

Synthesis of Chalcopyrite from Mixtures of Covellite and Pyrite at 58 mm. Pressure.—Pyrite and covellite powdered to grain size of 0.1 mm. and less were compressed into pellets, and samples were heated at various temperatures at 58 mm. pressure of sulphur vapor. The reaction progressed through several stages, which can be interpreted from the knowledge gained in making the diagram at 455 mm. Equilibrium was not reached in the 6-hour heatings, although with much finer grinding it might have been at the higher temperatures. The results are presented in Table 43 beginning with 420°, at which no reaction was observed, and heating new samples at progressively higher temperatures, the compound Cu_5FeS_6 and its solid solution ($Cu_{5+}FeS_{6+}$) formed at first, then at 10° to 15° below the temperature at which covellite changes to pure chalcocite, a chalcocite containing iron began to form. With rising temperature this chalcocite became richer in iron and grew at the expense of Cu_5FeS_6, as well as of covellite and pyrite. At still higher temperatures it reacted with pyrite to form first a copper-rich chalco-

pyrite and then a chalcopyrite of nearly theoretical composition.

The persistence of the larger grains of pyrite accounts for the slow progress toward equilibrium. For later work very fine grained mixtures of covellite and pyrite were produced by heating chalcopyrite or 1 : 1 mattes at temperatures of 400°–440° at 455 mm.

Sulphur was estimated from partial analyses, but the temperatures at which new phases appear are of more significance, especially if account is taken of the reverse reactions in which chalcopyrite absorbs sulphur at 58 mm. as described in the next section.

Reactions of Chalcopyrite at Various Temperatures at 58 mm. Pressure.—From Table 44 it is seen that at 58 mm. pressure near 570° chalcopyrite retains its proper amount of sulphur, but that it does not remain completely homogeneous. As temperature is lowered and new charges heated, absorption of sulphur and development of new phases take place. Chalcopyrite gives way to chalcocite solid solution and pyrite, then these and sulphur react to form Cu_5FeS_6, which in turn is replaced by covellite and pyrite.

With slight increase in sulphur the chalcocite formed goes into solid solution and is not present (unmixed) until the charges are cooled. At 525° the sample which had reacted least (37.8 per cent. sulphur) was still chalcopyrite. The other two samples, however, had reacted more and were largely chalcocite solid solution. Thus, 525° can be but little below the temperature at which chalcopyrite s. s. + sulphur → chalcocite s. s. + pyrite. The reverse change progressing in coarse grains at 550° must be considerably below 550° (Table 43). The compositions are not thus distinguishable from those with like phases at 550° for 455 mm. The textures of the chalcopyrite and the chalcocite solid solutions are quite different (Table 27).

The formation of Cu_5FeS_6 took place above 450°, but the reverse reaction could not be determined from the mixtures of covellite and pyrite because of nearly pure chalcocite that formed directly from covellite. However, the close spacing of compositions at 500–450° and then the abrupt absorption of sulphur at

450° indicates that the chalcocite solid solution that reacts with pyrite and sulphur to form Cu_5FeS_6 has a composition R_p, which the results do not distinguish from R at 455 mm.

The other reaction $Cu_{5+}FeS_{6+}$ + sulphur → covellite + pyrite must take place somewhat above 400°, and reverse somewhat below 430°.

At 10 mm.

At 10 mm. a sample of chalcopyrite heated for 6 hours at 475° absorbed about 5 per cent. of sulphur (sulphur percentage 39.6) and changed to chalcocite solid solution and pyrite. This is the same change that takes place at the equilibrium temperature 550° at 455 mm. Another sample heated 6 hours at 530° contained pyrite, and a recrystallized chalcopyrite with an intricate pattern of segregated chalcocite solid solution. In many other samples similarly heated at 10 to 25 mm. reaction did not start. (See "Chalcopyrite.")

Compositions of Chalcocite and Pyrrhotite.

The covellite-chalcocite equilibrium (Table 10*A*) from 10 mm. to 760 mm. covers less than 100°. The composition of the covellite is CuS, but the chalcocite contains an excess of sulphur—$Cu_2S_{1.15}$ has been obtained by observation and extrapolation at 497° for 760 mm. (Table 14). Other data along the dissociation pressure curve are lacking, but at constant pressure sulphur is expelled by heating (Table 14).

Similarly, pyrrhotite contains excess sulphur[14] (composition, in Table 15, on the equilibrium curve 677°–690°, $FeS_{1.19}$).

MELTING.

At the pressure 455 mm., each ratio of copper to iron has a definite composition with respect to sulphur at which with rising temperature liquid sulphide appears. These compositions form a continuous series which on a triangular diagram (Fig. 2) may be called the melting boundary. Our work and the work of

[14] Roberts (ref. 22) cites an inferred composition, $FeS_{1.25}$.

others as presented in Table 42 permit the approximate location of this line. No method has yet been used which preserves accurately for analysis the compositions of sulphides involving the solid solution of sulphur that melt at equilibrium.

The melting temperature of chalcocite is lowered, and of pyrrhotite raised by increasing sulphur. The observations of Dr. E. T. Allen,[15] quoted below, taken with ours in Table 45 show that increasing sulphur lowers the melting of the solid solutions having Cu : Fe = 1 : 1.

Meltings were made in thick-walled clear silica-glass tubes of about 1 cc. volume. About 0.5 g. of the powdered sulphide was used, and melting temperatures determined by observing when flowage occurred as the temperature was raised. Chalcopyrite from two sources, when melted, deposited in the tube quenched in water about 1 per cent. of sulphur. The sulphide melted at 875° ± 10°. With different bornites, melting was observed at temperatures between 950° and 1025°, and very little sulphur was seen condensed in the tubes. Cubanite was intermediate between chalcopyrite and bornite with respect to the amount of sulphur given off, and it began melting at about 910°. Pyrite had not melted at 1040°. Covellite changed to chalcocite which then melted below 1000°.

PHASE CHANGES IN THE SOLID STATE DURING COOLING.[16]

Cooling of preparations was not rapid enough to prevent some inversions and unmixing. No detailed characterization of these changes is here attempted, but several sets of experiments were made as aids in determining equilibrium at elevated temperatures. Some of the results are shown in Table 43.

In Chalcocite Solid Solutions.

Chalcocite solid solutions extending directly toward FeS are stable near their melting temperatures, but when cooled, *metallic copper*[17] separates, roughly in proportion to the iron present in

[15] Personal communication.

[16] For experiments and examples relative to ore minerals see G. M. Schwartz, ECON. GEOL., vol. 26, p. 739, 1931; vol. 27, p. 533, 1932, and Hermann Borchert, Chem. d. Erde, vol. 9, p. 145, 1934.

[17] About 4 per cent. metallic iron soluble in copper just below melting may separate on cooling. (Ruer and Goerens, Ferrum, vol. 14, p. 49, 1916.) See Tables 2 and 3.

the solid solution, nearly 7 per cent. was estimated microscopically (Table 2). Below the line F-Cu_2S on Fig. 2 metallic copper has been observed (Tables 16–18). Usually it forms hair-like growths on free or broken surfaces, always (?, Table 2) of the chalcocite solid solution.[18] 3:1 mattes have been observed repeatedly to show no copper when first taken from the crucible as hard cakes, but on standing the cakes became friable and little tooth-like tufts of copper hairs appeared in the cracks.[19]

At temperatures above about 170° chalcocite solid solutions rich in iron and sulphur unmix when cooled rapidly from above 480° into chalcocite solid solutions poorer in iron, and chalcopyrite solid solutions. (Tables 13 and 14, field M-F-K-N, and adjacent fields.) Unmixing at lower temperatures at ratios of Cu to Fe of 5:1, 6:1, 7:1 is shown in Table 43.

At temperatures below about 170°–200° the point Cu_5FeS_4 represents the mineral, bornite. Chalcocite solid solutions formed at higher temperatures and having compositions between Cu_5FeS_4 and iron-free chalcocite unmix forming bornite and less iron-rich chalcocites. These solid solutions richest in sulphur and iron[20] give also some chalcopyrite, and they recrystallize more coarsely (Table 43).

Chalcocite solid solutions near Cu_2S carried through the temperature range 85°–150° recrystallize because of inversion. Some products show a distinct pattern of two phases, others an indistinct mottling.[21] Increase of iron leads to increased color differences, increase of sulphur may prevent inversion. Our de-

[18] From one of our melts of Cu_2S + FeS in sealed silica glass without a graphite container, on cooling, the copper appeared suddenly at dull redness around the whole lump. H. Tiedemann ascribed marked changes in the electrical conductivity of cooling lumps of mattes between 548° and 180° to the formation of hair copper. (Metall und Erz, vol. 23, p. 200, 1926.)

[19] J. Wash. Acad. Sci., vol. 7, p. 196, 1917.

[20] G. M. Schwartz has made textural studies of natural mixtures variously heated and quenched, on or near the lines (*a*) Cu_5FeS_4-$CuFeS_2$ (Econ. Geol., vol. 26, p. 186, 1931), (*b*) $CuFeS_2$-$CuFe_2S_3$ (Econ. Geol., vol. 22, p. 44, 1927).

[21] For study of iron-free chalcocites see The Sulphides of Copper, E. Posnjak, E. T. Allen and H. E. Merwin, Econ. Geol., vol. 10, p. 491, 1915; and for geology see Alan M. Bateman and S. G. Lasky, Econ. Geol., vol. 27, p. 52, 1932.

Carpenter and Hayward (Ref. 2) indicate an inversion near 950°.

scriptions of the preparations from Cu to Fe ratios ∞ : 1 to 3 : 1 in Tables 2–7, 9, 10, 16–18, 21, 24, 28, 32, 33 are necessarily very general.

In Chalcopyrite-Cubanite Solid Solutions.

Chalcopyrite solid solutions and chalcocite solid solutions, each with variable sulphur content, extend nearly far enough to meet near 2.6 : 1 ratio of Cu : Fe. Our comparatively slow quenchings did not prevent unmixing, except that between about 1.1 : 1 and 1 : 1 no unmixing was detected. (See Table 43 and discussion of Tables 24 to 28.)

The line [20] of solid solutions between $CuFeS_2$ and $CuFe_2S_3$ has unmixed more readily than those solutions with the same Cu : Fe ratios containing less sulphur. (See Table 43.)

In Pyrrhotite Solid Solutions.

Melts of various pyrrhotites often become friable during cooling. This is probably caused by an inversion,[22] rather than differential contraction. At ordinary temperatures pyrrhotites containing more sulphur than $FeS_{1.1}$ are very magnetic, others are weakly magnetic (Table 15).

ACKNOWLEDGMENTS.

Contributions were kindly made to this study by Professor L. C. Graton by furnishing mineral specimens, and by our colleagues Dr. G. W. Morey and Dr. George Tunell by discussing with us phase rule theory relating to experiments near the 550° isotherm.

SUMMARY.

For Cu, Fe and S at temperatures not far below melting the compounds lowest in sulphur are Cu_2S and FeS. Between these

[22] Fedotieff (Ref. 11) ascribes a heat effect near 830° to inversion. Others have discussed evidence of an inversion near 100° (see below), but cf. our results on the insolubility of iron in FeS. H. S. Roberts has made a detailed thermal study of transformations in the FeS-S solid solutions. J. Am. Chem. Soc., vol. 57, p. 1034, 1935.

are: (1) considerable solid solution at the Cu_2S end, (2) a little solid solution at the FeS end, (3) mixtures of these solid solutions. Their dissociation pressure of sulphur is a fraction of a millimeter of mercury, therefore if powdered mixtures of the sulphides are heated in sulphur vapor at higher pressures, sulphur is absorbed. The first effect is the formation of sulphur-rich solid solutions, $Cu_2(Fe)S_{1+}$ (chalcocites) and $Fe(Cu_2)S_{1+}$ (pyrrhotites); the second, the production of five ternary compounds all of which are subject to solid solution; and the third, the formation of the two binary compounds covellite (CuS) and pyrite (FeS_2), which do not show appreciable solid solution, and are stable even in contact with saturated sulphur vapor over a wide range. Two of the ternary compounds, Cu_5FeS_6 and $Cu_3Fe_4S_6$(?) are new. For some of these reactions the temperatures and pressures of sulphur vapor at a few pressures have been found, thus establishing dissociation pressure curves for Cu_5FeS_6, Cu_5FeS_4 (bornite), $CuFe_2S_3$ (cubanite), and $CuFeS_{1.94}$ (chalcopyrite solid solution).

At 455 mm. Pressure of Sulphur Vapor on a triangular diagram of compositions, data obtained below the temperature of the beginning of melting of the sulphide powders and above the temperature of condensation of the sulphur vapor were plotted, from which the following may be summarized. From many series of analytical compositions at particular temperatures isotherms were drawn. From changes in direction of the isotherms and from the solid phases present, fields containing the same phases were outlined. Fields of solid solution contain a single solid phase, and are crossed by slightly curved isotherms. Pyrrhotite solid solution covers the range of highest temperature from incipient melting at *ca.* 1185°, to 675°, where it reacts with sulphur to form pyrite and intermediate solid solution. Intermediate solid solution melts (or reacts with liquid) near 950° and reacts with sulphur to form pyrite and chalcocite solid solution at 550°. Chalcocite solid solution melts at *ca.* 1085° and reacts with sulphur to form covellite and $Cu_{5+}FeS_{6+}$ solid solution at 472°. Cu_5FeS_6 forms at 484°, and its solid solution reacts

with sulphur to form pyrite and covellite at *ca.* 445°. Pyrrhotite solid solution extends only a few per cent. toward S and Cu_2S; intermediate solid solution is about 3 per cent. wide with respect to sulphur, over the middle fourth of the triangle; and likewise chalcocite solid solution extends as a strip about 1½ per cent. wide, half-way to the middle of the triangle.

Between solid solutions that approach each other there are fields in which both solid solutions are present. In these fields the isotherms are sub-parallel straight lines joining the two compositions that are stable together. The temperature ranges in these (three) fields between solid solutions are: pyrrhotite-intermediate, *ca.* 920°–675°; intermediate-chalcocite, *ca.* 925°–550°; chalcocite-$Cu_{5+}FeS_{6+}$, 48_4°–472°.

Five other fields of two solid phases appear. They are between other parts of the boundaries of these solid solutions and the definite compounds pyrite and covellite. These fields are wedge-shaped. Two boundaries and the isotherms radiate as straight lines from the compounds.

In case three solid phases take part in a reaction they are stable together in any proportions and at a single temperature. Thus, in the composition triangle the straight lines joining the compositions of the three reacting solids outline a triangular isothermal field. Five such fields have been found at the following temperatures: 675°, 55_0°, 48_4°, 472°, 44_5°.

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TABLE 1. COMPOUNDS.

		Composition Wt. %.				
		Cu.	Fe.	S.	Color of Compounds.*	Relative Hardness.
Chalcocite	Cu_2S	79.86	—	20.14	Gray *	Soft
Covellite	CuS	66.48	—	33.52	Light blue to dark blue	Soft
Pyrrhotite	FeS	—	63.53	36.47	Light yellow *	Hard
Pyrite	FeS_2[a]	—	46.55	53.45	Yellowish white	Very hard
Chalcopyrite	$CuFeS_2$	34.64	30.42	34.94	Bright yellow *	Medium
Cubanite	$CuFe_2S_3$	23.42	41.14	35.44		Medium
(New compound)	$Cu_3Fe_4S_6$	31.45	36.83	31.72		Medium
Bornite	Cu_5FeS_4	63.32	11.13	25.55	Grayish yellow-orange	Soft
(New compound)	Cu_5FeS_6	56.15	9.87	33.98	Bronze, or bright yellow to grayish orange *	Soft

* Colors of solid solutions are described in the text. In the tables *chalcocite solid solutions* are described as gray, bluish-gray, neutral-gray, orange, and as homogeneous or mottled. Mottling is a general term for more or less indefinite, and fine-grained color differences which develop during cooling. Near an indefinite boundary (Table 18) these mottlings disappear or become unnoticeable, and the products have been called "homogeneous." Slow cooling might extend the range of the mottling. *Pyrrhotite solid solutions* are called hard yellow; *intermediate solid solutions*, soft yellow; and the compound Cu_5FeS_6, bronze-colored. Obvious contractions and abbreviations appear.

[a] Concerning marcasite see Table 41*A*.

TABLE 2. Cu_2S + FeS* MELTED TOGETHER IN EVACUATED TUBES AT ABOUT 1170°.

Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Description of Phases, and Remarks (see Tables 1 and 8).
Cu_2S 1.000	79.86	—	20.14	Practically homogeneous gray.
Cu_2S 0.9982	79.89	—	20.11	Practically homogeneous gray (minute trace Cu).
—	79.18	0.52	20.30	Gray, no mottling, a little capillary Cu, no Fe.
—	78.11	1.51	20.38	Gray, grid-like mottling and capillary Cu, no Fe.
24 : 1	76.42	2.75	20.83	Gray, mottled grid-like structure + Cu, capillary.
13 : 1	73.50	5.13	21.37	Gray, mottled sulphide + capillary Cu, no Fe.
9 : 1	Not analyzed		—	Gray, mottling uncertain, Cu, no Fe.
6 : 1	67.56	9.88	22.56	Faintly mottled sulphide + Cu, capillary.
5 : 1	65.39	11.57	23.04	Mottled sulphide + Cu, capillary.
5 : 1	65.37	11.53	23.10	Mottled sulphide + capillary Cu, no Fe.
5 : 1	65.36	11.61	23.03	Mottled sulphide + Cu, capillary.
5 : 1	65.57	11.52	22.91	Mottled sulphide + Cu, capillary, and trace inside grains, microscopical estimation 7% or less, no Fe.
4 : 1	62.19	13.87	23.94	Mottled sulphide + Cu + Fe.
4 : 1	62.89	13.65	23.46	Mottled orange + Cu, capillary and inside grains, + trace Fe.
3.5 : 1	60.72	15.21	24.07	Mottled orange + trace hard yellow + Cu, capillary and inside grains, + trace Fe.
3 : 1	58.28	17.15	24.57	Mottled orange + *ca.* 5% hard yellow + Cu, capillary and inside grains, + < 1% Fe.
2 : 1	51.24	22.81	25.95	Coarsely mottled orange + hard yellow + Cu, capillary and inside grains, + Fe.
1 : 1	38.12	33.43	28.45	Coarsely mottled orange + hard yellow + Cu, capillary and inside grains, + Fe.
1 : 2	24.88	43.73	31.39	Mottled orange + much hard yellow + Cu, capillary and inside grains, + a little Fe, some eutectoid structure.
1 : 5	12.43	53.85	33.72	Hard yellow + orange + a little Cu + trace Fe.
1 : 10	6.55	58.29	35.16	Hard yellow + *ca.* 3% interstitial orange + traces Fe + trace Cu.
—	2.0	Not analyzed	—	Hard yellow + traces Fe, no orange.
FeS 1.002	—	63.48	36.52	Hard yellow + trace Fe (0.01%).
FeS 0.9883	—	63.80	36.20	Hard yellow, Fe probably present.

* FeS .9883 used in some.

Table 2.—Very little dissociation into metals and sulphur-rich sulphides is shown for crystallizing mixtures of Cu_2S and FeS. Metallic iron in excess of 1 per cent. has not been noted. Copper of early formation and mossy copper filling inner cavities are not always distinguishable, but in the one sample selected by inspection as having most total copper, practically all the copper was mossy, and because of porosity would be over-estimated in polished section. It consists of snarled fibers .002–.003 mm. in diameter. The rate of cooling affects the amount and the character of the growth. When it is present, usually all exposed surfaces of the chalcocite solid solution show it, but from one melt of bornite, considerably deficient in sulphur, protruding cubo-octahedrons had copper on the octahedron only. In a single instance capillary copper was noticed on, or possibly protruding through, the thin lamellæ of the intermediate solid solution, such as $2\frac{1}{2}$: 1 of Table 8.

TABLE 3. Cu_2S 1.016 + FeS 1.036 MELTED TOGETHER IN EVACUATED TUBES AT ABOUT 1170°.

Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.*	Description of Phases, and Remarks (see Tables 1 and 8).
Cu_2S 1.016	79.60	—	20.40[a]	Homogeneous, gray, neither mottling nor Cu.
—	77.75	1.44	20.81	Practically homogeneous, gray, trace of mottling, no Cu or Fe.
—	75.72	3.11	21.17	Coarse reticulate mottled, a little Cu, capillary and inside grains, no Fe.
—	71.90	6.06	22.04	Reticulate mottled sulphide + capillary Cu, no Fe.
6 : 1	67.19	9.74	23.07	Gray sulphide with 2 kinds of mottling, + capillary Cu, no Fe.
5 : 1	65.06	11.58	23.36	Mottled orange sulphide + capillary Cu, no Fe.
4 : 1	62.17	13.72	24.11	Mottled orange sulphide + Cu, capillary and inside grains, + about 1% hard yellow.
3.5 : 1	60.14	15.26	24.60	Mottled orange + about 4% evenly distributed hard yellow + Cu + trace Fe.
3 : 1	58.00	16.88	25.12	Mottled orange + hard yellow + Cu, capillary and inside grains, + traces Fe.
3 : 1	57.80	17.06	25.14	Mottled orange + hard yellow + Cu, capillary and inside grains, no Fe.
2 : 1	51.17	22.42	26.41	Orange + hard yellow + Cu, capillary and inside grains, no Fe.
1 : 1.3	32.49	37.21	30.30	Orange + hard yellow + capillary Cu, no Fe + a little eutectic.
1 : 5	12.28	53.15	34.57	Hard yellow + a little orange + traces Cu, no Fe.
FeS 1.036	—	62.70	37.30[a]	Homogeneous, hard yellow.

* In all but end members sulphur 0.1–0.2% low, see Table 4.
[a] Not melted separately.

TABLE 4. Cu_2S 1.042 + FeS 1.082 MELTED TOGETHER IN EVACUATED TUBES AT ABOUT 1170°.

Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Description of Phases, and Remarks (see Tables 1 and 8).
Cu_2S 1.042	79.20	—	20.80*	Gray, finely but distinctly mottled.
3 : 1	57.61	16.97	25.42	Orange, not mottled, + long gashes soft yellow + long gashes Cu, no Fe.
1.5 : 1	45.20	26.62	28.18	Orange, not mottled, + clear grains and coarse gashes soft yellow + gashes Cu + little hard yellow, no Fe.
1 : 1⅓	31.82	37.06	31.12	Orange + hard yellow and soft yellow in nearly equal amounts + few stringers of Cu, no Fe.
FeS 1.082	—	61.69	38.31*	Homogeneous, hard yellow.

* Analyses of mattes 2 and 51 of Table 5. These mattes were mixed for the intermediate members, but were not melted separately. The latter when melted contained about 0.2 per cent. more sulphur than shown by the analyses, which condensed in the tubes during cooling.

Tables 3 and 4.—The 3 : 1 product in Table 4 contains only slightly more sulphur (0.3 per cent.) than the one of Table 3, but enough to prevent the formation of pyrrhotite (hard yellow). The extra iron thus held in the chalcocite solid solution (orange) separated during cooling as the more sulphur-rich soft yellow (intermediate) solid solution. The separation of metallic copper, and the attendant enrichment in sulphur and iron of the remaining chalcocite solid solution, augmented the amount of this yellow constituent. Both of these unmixings are affected by the rate of cooling.

TABLE 5. COMPOSITIONS AND PROPERTIES OF COPPER-IRON MATTES MELTED IN HYDROGEN SULPHIDE AT 1080° TO 1250°.

No.[1]	Cu : Fe (Molal).	Temp. ° C.	Composition Wt. %. Cu.	Fe.	S.	No. of Melt.	Description of Phases, and Remarks (see Tables 1, 8, and 17A).
1	1 : 0	1130	79.16	—	20.84	—	Homogeneous = Cu_2S 1.044.
2	1 : 0	1170	79.20	—	20.80	—	Homogeneous to minutely mottled; faintly blue
3	—	1170	77.84	1.07	21.09	4th	Homogeneous.
4	29 : 1	1170	76.11	2.32	21.57	—	Homogeneous, gray.
5	16.3 : 1	1170	73.90	3.97	22.13	3rd	Homogeneous; faintly orange, darker
6	11 : 1	1120	71.45	5.69	22.86	4th	Homogeneous; than Cu_2S
7	9.7 : 1	1200	70.81	6.43	22.76	4th	Non-homogeneous, very fine mottling in some grains.
8	8.5 : 1	1170	69.69	7.18	23.13	4th	Homogeneous.
9	7.8 : 1	1170	68.89	7.78	23.33	4th	Non-homogeneous, mottled.
10	6.9 : 1	1170	67.69	8.64	23.67	5th	Non-homogeneous (?) mottling very obscure.
11	6.2 : 1	1170	66.67	9.42	23.91	3rd	Homogeneous.
12	6 : 1	1170	66.26	9.72	24.02	2nd	Traces of mottling.
13	5.3 : 1	1170	64.91	10.76	24.33	4th	Non-homogeneous, mottled.
14	5 : 1	1170	64.43	11.11	24.46	4th	Non-homogeneous, mottled.
15	4.6 : 1	1170	63.04	12.15	24.81	5th	Non-homogeneous, mottled, slight capillary Cu, about 20 per cent. of coarse gash-to-veinlike gray in orange. Blue with NHO_3.
16	4 : 1	1170	61.22	13.50	25.28	5th	Partly mottled + capillary Cu.
17	3.7 : 1	1100	59.98	14.42	25.60	6th	Homogeneous orange + capillary Cu.
18	3 : 1	1080	57.00	16.68	26.32	4th	Homogeneous orange + capillary Cu on standing.
19	3 : 1	1170	57.10	16.72	26.18	4th	Homogeneous + a little capillary Cu.
20	2.7 : 1	1170	55.47	17.91	26.62	4th	Orange + about 5 per cent. soft yellow coarse gashes + capillary Cu.

TABLE 5 (*Continued on next page*)

TABLE 5 (*Continued*).

No.[1]	Cu : Fe (Molal).	Temp. °C.	Composition Wt. %. Cu.	Fe.	S.	No. of Melt.	Description of Phases, and Remarks (see Tables 1, 8, and 17A).
21	2.5 : 1	1170	54.10	19.00	26.90	4th	Orange + about 10 per cent. soft yellow gashes + capillary Cu.
22	2 : 1	1080	50.52	21.65	27.83	4th	Orange + soft yellow gashes + capillary Cu *after standing.*
23	1⅔ : 1	1100	46.85	24.57[d]	28.58[d]	6th	Orange + soft yellow grains and gashes + capillary Cu.
24	1.5 : 1	1200	44.72	26.17	29.11	4th	Orange + soft yellow blebs + capillary Cu.
25	1.3 : 1	1080	42.05	28.04	29.91	6th	Orange blebs and gashes in soft yellow, + Cu.
26	1.09 : 1	1170	38.62	31.20	30.18[c]	4th[a]	About ⅛ orange coarse gashes + ⅞ soft yellow + capillary Cu after standing.
27	1 : 1	1170	36.80	32.34	30.86	9th[d]	Soft yellow + about 10 per cent. orange gashes + capillary Cu on standing.
28	1 : 1	1170	—	—	—	—	Chalcopyrite melted twice, soft yellow + orange, Cu after polishing.
29	1 : 1	1080	36.50	32.25	31.25	—	Chalcopyrite melted twice, soft yellow + orange + Cu after polishing.
30	1 : 1.2	1170	33.37	35.16	31.47	5th	Soft yellow + trace orange and hard yellow.
31	1 : 1⅛	1170	31.12	36.99	31.89	4th	Practically all soft yellow.
32	1 : 1⅓	1080	31.64	36.40	31.96	4th	Soft yellow + very little hard yellow.
33	1 : 1⅓	1250	31.40	37.08	31.52	6th	Soft yellow + some hard yellow + orange.
34	1 : 1⅜	1170	27.34	39.96	32.70	5th	Soft yellow + about 10 per cent. hard yellow + trace orange + Cu.
35	1 : 2	1250	23.95	43.08	32.97	—	Soft yellow + hard yellow + orange grains and streaks.
36	1 : 2	1170	24.10	42.70	33.20	9th	Soft yellow + about 20 per cent. hard yellow, no orange.
37	1 : 2¼	1170	22.24	44.12	33.64	4th	Soft yellow + hard yellow.
38	1 : 2¼	1170	22.07	44.17	33.76	4th	Soft yellow + hard yellow.
39	1 : 2.6	1170	20.07	45.71	34.22	4th	Soft yellow + hard yellow.
40	1 : 2.7	1170	19.57	46.17	34.26	4th	Hard yellow + soft yellow.
41	1 : 3.2	1170	17.29	48.22	34.49	4th	Hard yellow + soft yellow.
42	1 : 3.6	1170	15.51	49.67	34.82	4th	Hard yellow + soft yellow.
43	1 : 4	1170	14.47	50.25	35.28	3rd	Hard yellow + soft yellow.

TABLE 5 (*Continued on next page*)

TABLE 5 (*Continued*).

No.[1]	Cu : Fe (Molal).	Temp. ° C.	Composition Wt. %. Cu.	Fe.	S.	No. of Melt.	Description of Phases, and Remarks (see Tables 1, 8, and 17A).
44	1 : 10	1170	6.39	56.85	36.76	4th	Hard yellow + some soft yellow.
45	1 : 19	1140	3.46	58.96	37.58	2nd	Hard yellow + a little soft yellow.
46	1 : 36	1200	1.92	60.39	37.69	3rd	Hard yellow.
47	1 : 67	1170	1.04	60.90	38.06[a]	3rd	Hard yellow.
48	0 : 1	1200	—	62.94	37.06	2nd	Hard yellow = FeS 1.023.
49	0 : 1	1170	—	61.93	38.07[a]	3rd	Hard yellow = FeS 1.071.
50	0 : 1	1230	—	62.51	37.49	3rd	Hard yellow = FeS 1.045.
51[b]							

[1] Most of the numbered mattes, 1–74 of Tables 5, 7, 8 contain less sulphur than the equilibrium preparations of the rest of the tables. If the mattes have been specially prepared or treated to make the sulphur content high so that equilibrium could be approached from the high-sulphur side, an "h" or "H" or a temperature at which a preheating was made (602), $_{400}$ are added.

[a] Had not melted.

[b] See end of Table 7. List continued Table 8.

[c] First melt after metallic lump or shell disappeared.

[d] Third melt after adding metallic copper.

Table 5.—The mattes of Tables 5, 7, and 8 reached their content of sulphur in a stream of hydrogen sulphide during repeated melting, crystallization and powdering of preparations, to some of which powdered sulphur had been added. At low temperatures surface reactions on grains increased the sulphur content, which then tended to lessen at higher temperatures, especially above melting. A uniform procedure, with no sulphur added to the last two melts, involving a long series between Cu_2S_{14} and FeS_{14} resulted in a nearly straight line of compositions (Table 17A). Heating to less than 1170° produced mattes richer in sulphur, higher heating lowered the sulphur.*

* See p. 219 for heating $Cu_3Fe_4S_6$, and compare the following mattes: Nos. 6 and 7; Nos. 18 and 19; Nos. 31 and 32. Note that No. 25 at 1080° has about 0.3 per cent. more sulphur, and No. 35 at 1250° about 0.4 per cent. less sulphur than corresponds to 1170°. Several incidental analyses not here recorded show 0.2 to 0.5 per cent. difference for 100°, and the later studies of equilibrium indicate 0.2 to 0.3 per cent.

By our method of preparation part of the added sulphur that boiled out condensed in the upper part of the tube containing the crucible. Undoubtedly vapor from this sulphur was not entirely excluded from the crucible by the hydrogen sulphide. If sulphur was added to the last melt, toward the copper end of the series, about 1½% more was retained than by the usual procedure, but toward the iron end (beyond 1 : 1⅓) a much less excess caused spewing as the melt crystallized. Although this series of compositions is closely reproducible, it can not be accurately related to a definable equilibrium.

The various lots of Merck's ferrous sulphide used contained from 67 to 70 per cent. of iron. FeS contains only 63½ per cent. The discrepancy is not accounted for by the small amount of free iron. The grains of pyrrhotite were embedded in a very fine eutectic of pyrrhotite and an abundant hard dull-gray constituent which disappeared slowly during heating in hydrogen sulphide or sulphur vapor. In a heating of a fine powder for 12 hours at 850° in sulphur vapor at 455 mm. pressure most of it disappeared and the enclosing tube contained SO_2. Evidently the material was iron oxide. (See p. 209.)

TABLE 6. ILLUSTRATING THE PROGRESSIVE INCREASE OF SULPHUR, AND THE CORRESPONDING PHASE CHANGES WHICH OCCUR WITH SUCCESSIVE MELTINGS DURING THE PREPARATION OF THE MATTES IN HYDROGEN SULPHIDE.

Cu : Fe (Approx.).	Composition Wt. %. Cu.	Fe.	S.	No. of Melt.	Description of Phases, and Remarks (see Table 1).
2 : 1	52.76	24.18	23.06	2nd	Mostly orange, a little hard yellow, Cu. Fe.
	50.52	21.65	27.83	4th	Orange + soft yellow + little Cu.
1 : 1	37.64	33.82	28.54	2nd	About ½ and ½ orange + hard yellow + Cu + Fe.
	36.35	32.89	30.76	4th	Soft yellow + about 10 per cent. orange.
1 : 1.2	38.22	34.40	27.38	2nd	Orange + hard yellow + Cu + Fe.
	33.51	35.52	30.97	3rd	Orange + hard yellow + soft yellow + Cu.
	33.37	35.16	31.47	5th	Soft yellow and trace of orange and hard yellow.
1 : 1⅓	32.77	40.80	26.43	1st	Orange + hard yellow + *ca.* 4 per cent. Cu, + Fe + oxide.
	32.63	37.51	29.86	2nd	Orange + hard yellow + traces Cu and Fe.
	31.22	36.98	31.80	3rd	Mostly soft yellow + traces of hard yellow, orange and Cu.
	31.64	36.40	31.96	4th	Soft yellow + trace hard yellow.
1 : 4	14.97	54.43	30.60	1st	Hard yellow + orange + Cu + Fe + oxide.
	14.47	50.25	35.28	3rd	Hard yellow + soft yellow.

TABLE 7. COMPOSITION AND PROPERTIES OF COPPER-IRON MATTES. Mattes mixed with excess sulphur before melting in hydrogen sulphide.

No.[1]	Cu : Fe (Molal).	Temp. °C.	Composition Wt. %. Cu.	Fe.	S.	No. of Melt.	Description of Phases, and Remarks (see Table 1).
72	Cu_2S 1.122	1090	77.95	—	22.05	2nd	Bluish gray.
73	6 : 1	1080	64.58	9.58	25.83	2nd	Homogeneous, orange.
74	4 : 1	1080[a]	59.97	13.05	26.99	3rd	Orange + soft yellow.
65	2⅓ : 1	1050	50.13	20.76	29.11	2nd	Soft yellow + orange (see Table 8).
51	0 : 1	1250	—	61.69	38.31	3rd	Sulphur added to last melt.

[1] See note, Table 5.

[a] The 4 : 1 matte made by adding excess sulphur before melting has practically the same composition and phases as the one of Table 28, heated at 540° with sulphur vapor pressure 455 mm.

TABLE 8. COPPER-IRON MATTES. CONDITIONS OF PREPARATION INCOMPLETELY RECORDED.

No.[1]	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	No. of Melt.	Description of Phases, and Remarks (see Table 1).
52	17 : 1	72.98	3.69	23.33 [h]	1st	Homogeneous, gray.
53	14 : 1	71.72	4.55	23 73 [h]	1st	Homogeneous, gray.
54	9 : 1	68.54	6.89	24.57 [h]	2nd	Homogeneous, gray.
55	7 : 1	66.61	8.43	24.96 [h]	1st	Homogeneous, brownish gray.
56	7 : 1	67.68	8.40	23.92	2nd	Homogeneous, brownish gray.
57	6 : 1	66.12	9.60	24.28	2nd	Minutely mottled.
58	6 : 1	66.25	9.66	24.09	3rd	Minutely mottled.
59	5 : 1	64.60	11.41	23.99 [l]	1st	— —
60	5 : 1	64.30	11.17	24.53	5th	Minutely mottled.
61	5 : 1	63.04	11.08	25.88 [h]	2nd	Homogeneous, grayish orange.
62	4.5 : 1	62.78	12.30	24.92	2nd	Minutely mottled.
63	4 : 1	61.42	13.41	25.17	3rd	— —
64	3 : 1	56.10	16.58	27.32 [h]	2nd	Grayish orange with about 10 per cent. soft yellow streaks. variable.
65	2⅛ : 1	50.13	20.76	29.11 [h]	2nd	Orange-streaked soft yellow in orange.
65A	2 : 1	50.12	22.39	27.49 [l]	3rd	Grayish orange + soft yellow.
66	1 : 1	36.84	32.59	30.57	4th	Soft yellow with orange streaks.
67	1 : 2	24.09	42.52	33.39	5th	Soft yellow with little hard yellow.
68	1 : 2	24.06	42.46	33.48	5th	Soft yellow with little hard yellow.
69	1 : 3	17.58	47.28	35.14 [h]	4th	Soft yellow + hard yellow.
70	1.: 4	13.68	50.53	35.79 [h]	2nd	Hard yellow + soft yellow.
71	1 : 5	12.26	52.30	35.44 [l]	2nd	Hard yellow + soft yellow + oxide.
72	List continued in Table 7.					

[1] See note, Table 5.

[h, l] Sulphur is about 0.5 to 1.5 per cent. higher and lower, respectively, than in mattes of Table 5.

Tables 2 to 8.—Chalcocite solid solutions free of iron form cubo-octahedrons in melts, likewise in sulphur vapor at various temperatures as low as 280°, while from melts, if sulphur-rich, an octahedral parting develops. (Posnjak, Allen and Merwin, ECON. GEOL., vol. 10, 507 and 521, 1915.) From melts containing iron, faceted areas often protrude, and pipes and vugs have crystal linings, exhibiting cubo-octahedrons. Lamellæ of chalcopyrite solid solution (unmixed) are parallel to the cube. (Details beyond.)

$Cu_5Fe_4S_8$ solid solutions rich in chalcocite (Matte 27) give evidence of being rhombohedral while crystallizing from melts. At high temperature chalcocite solid solution segregates from them in coarse lamellæ, and at somewhat lower temperature these are fractured and offset. The symmetry relations lead to the conclusion that the lamellæ are rhombohedral and the fracture planes basal, but accurate measurements are not possible. Fragments show glistening separation planes or striations parallel to such planes. On the planes minute interrupted fractures form roughly equilateral triangles which are parallel to or coincident with outcroppings of orange-colored lamellæ. Polishing normal to the separation planes reveals the lamellæ at high angles. The *color* differences in these two solid solutions are more pronounced as the sulphur contents increase.

The lumps of *chalcocite* solid solutions 8.7 : 1 and 5 : 1 of Table 5 had protruding cubo-octahedrons, while the 6 : 1 contained a pipe, and the 2⅛ : 1 (Table 8) a vug. A group from the latter consisting of several parallel crystals showing octahedron, cube, and dodecahedron was measured, then ground and polished along an octahedral

plane. Yellow streaks paralleled the octahedral edges, but on corners of broken pieces of matte yellow streaks formed the outcrops of thin plates arranged in three rectangular directions. Polishing parallel to a reflecting surface of separation in one of these directions revealed a rectangular pattern of coarse yellow stripes about 0.02 mm. wide. These were finely streaked with orange, roughly parallel to their lengths, resulting from a second unmixing, which, in more sulphur-rich preparations, takes place below 560° (see Table 27). In a 3 : 1 matte yellow lamellæ followed cube planes.

A small vug in 2⅛ : 1 lined with uniformly oriented crystals when sectioned parallel to the cube showed that the interstitial liquid last to crystallize was still within composition limits of the chalcocite solid solution. Matte 65*A* with 1½ per cent. less sulphur was similar, but No. 24, 1½ : 1, quite evidently did contain two original constituents and also No. 23, 1⅔ : 1.

Commonly as mattes solidified sulphur boiled out, sometimes leaving the matte porous, sometimes producing a scoriaceous surface.

TABLE 9.

(*a*) HEATINGS AT 925°, 2 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1, 8, 17A).
($CuFeS_2$[k])	1 : 1	36.73	32.38	30.89	2	Soft yellow + a little orange.
30[H]	1 : 1.2	33.22	35.16	31.62	2	Soft yellow + trace hard yellow, and orange streaks.
32[H]	1 : 1⅛	31.51	36.50	31.99	2	Soft yellow + a little hard yellow + a little orange.
34[H]	1 : 1⅔	27.52	39.69	32.79	2	Soft yellow + a little hard yellow.
36[H]	1 : 2	24.15	42.23	33.62	2	Soft yellow + 9 to 11 per cent. hard yellow.

(*b*) HEATINGS AT 900°, 2 MM.

(CuS[k])	∝ : 1	79.14	—	20.86*	2	Mottled gray, originally CuS, now Cu_2S 1.045.
52[k]	17.3 : 1	73.98	3.70	22.32†	2	Gray, no distinct mottling, no Cu.
53[k]	14 : 1	72.83	4.59	22.58†	2	Gray, no distinct mottling, no Cu.
54[k]	9 : 1	69.63	6.81	23.56†	2	Gray, no distinct mottling, no Cu.
55[k]	7 : 1	67.33	8.53	24.14†	2	Gray, no distinct mottling, no Cu.
61[k]	5 : 1	64.02	11.31	24.67*	2	Coarsely mottled orange and gray.
74[k]	4 : 1	60.94	13.26	25.80†	2	Finely mottled orange and gray, no Cu.
64[k]	3 : 1	56.91	16.71	26.38*	2	Finely mottled orange + trace Cu + trace soft yellow gashes.
65[k]	2⅛ : 1	51.13	21.26	27.61*	2	Finely mottled orange + trace Cu + *ca.* ⅛ soft yellow grains.
($CuFeS_2$[k])	1 : 1	36.56	32.26	31.18*	2	Soft yellow + a little orange in streaks, + trace Cu after standing.

TABLE 9 (*Continued on next page*)

TABLE 9 (*Continued*).

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1, 8, 17A).
($CuFeS_2$[h])	1 : 1	36.57	32.37	31.06	2	Soft yellow + a little orange in gashes, no Cu at first.
30[H]	1 : 1.2	33.20	35.12	31.67*	2	Soft yellow + hard yellow.
32[H]	1 : 1⅓	31.45	36.48	32.07*	2	Soft yellow + trace hard yellow and Cu.
34[H]	1 : 1⅔	27.45	39.59	32.96	2	Soft yellow + 5 per cent. hard yellow.
36[H]	1 : 2	24.12	42.14	33.74	2	Soft yellow + 16 per cent. hard yellow.
		(*c*) 3-HOUR HEATINGS AT 880° IN H_2S.				
30	1 : 1.2	32.90	34.86	32.24	1	Soft yellow only.
32	1 : 1⅓	31.07	36.02	32.91	1	Soft yellow only.
34	1 : 1⅔	27.26	39.21	33.53	1	Soft yellow + a little hard yellow.
36	1 : 2	23.91	41.79	34.30	1	Soft yellow + *ca.* 1 per cent. hard yellow.

* See text.

[h] Sulphur higher } than in final product.
[l] Sulphur lower }

[H] Had been heated in H_2S at 880°, therefore had higher sulphur content than final product.

† Same heating, sulphur 0.2–0.4 per cent. high.

Table 9.—Twelve-hour heatings at 2 mm. pressure of sulphur vapor failed to bring some of the mattes high in sulphur down even to the compositions at the same temperature at 58 mm. (Table 10), therefore the study was not carried further. It is probable that the porous materials resulting from the desulphuration of covellite and chalcopyrite reacted nearly completely. A straight line joining these compositions comes near the compositions of the other products lowest in sulphur, and may represent approximately the 900° isotherm at 2 mm.

Powdered mattes 4 : 1 to 1 : 2 of the 1170° series of Table 5 heated in H_2S to about 880°, held at this temperature for about 20 minutes and then cooled in place in the furnace gained about 0.4 to 0.9 per cent. sulphur respectively. Holding at 880° for 3 hours did not materially increase the sulphur.

In the mattes of Tables 4 to 8, and also in the preparations at 900°—2 mm., the soft yellow constituent almost excludes the others near 1 : 1⅓. Thus, $Cu_3Fe_4S_x$ is evidently its composition, where x represents a percentage of sulphur between 32.1 and 29.8. The latter is on the line Cu_2S–FeS and represents the formula $Cu_6Fe_8S_{11}$. If this is the composition of this end member of the intermediate solid solution, it must be stable only at pressures of much less than 1 mm. and at temperatures far below melting. But the simpler formula, $Cu_3Fe_4S_6$, comes nearly within the range of temperatures and pressures already investigated.

Mattes in the vicinity of 1 : 1⅓ contain large grains of pyrrhotite. When the mattes are powdered some fragments consist largely of pyrrhotite. All fragments absorb sulphur readily but the interchange of copper and iron amongst grains may not be complete after two 6-hour heatings. Also, homogeneous solid solutions here lose sulphur more rapidly than the requisite pyrrhotite crystallizes out. Thus, the position of the boundary, Q–$CuFe_2S_3$, is only approximately represented by the percentages of pyrrhotite indicated in Table 9.

TABLE 10. ISOTHERM 900°, 58 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1, 8, 17A).
14[l]	5 : 1	64.21	10.99	24.80[a]	2	Mottled orange, no Cu.
61[h]	5 : 1	63.61	11.28	25.11[a]	2	Mottled orange, no Cu.
22[l]	2 : 1	50.16	21.67	28.17[a]	2	Orange-gray + soft yellow + trace of extruded Cu.
65[h]	2⅛ : 1	51.12	21.01	27.87[a]	2	Orange-gray + soft yellow grains and gashes + trace of extruded Cu.
23[l]	1⅜ : 1	46.29	24.45	29.26	2	Soft yellow grains and gashes in orange + trace of extruded Cu.
24[l]	1.5 : 1	44.19	25.80	30.01[b]	2	Soft yellow + orange patches and gashes + trace of extruded Cu.
25[l]	1⅛ : 1	41.88	27.94	30.18	2	Soft yellow + orange + trace of extruded Cu.
26[l]	1.09 : 1	38.27	30.70	31.03	2	Soft yellow + orange gashes + a little extruded and enclosed Cu.
($CuFeS_2$[h])	1 : 1	36.37	32.05	31.58[a]	2	Soft yellow.
68	1 : 2	—	—	—	1	Originally soft yellow. Now soft yellow + hard yellow.
67	1 : 2	—	—	—	1	Originally soft yellow + hard yellow. Now soft yellow + hard yellow.
37[l]	1 : 2¼	21.88	43.61	34.51	2	Soft yellow + hard yellow.
39[l]	1 : 2.5	19.88	45.11	35.01	2	Soft yellow + hard yellow.
41[l]	1 : 3.2	16.85	47.38	35.77	2	Soft yellow + hard yellow.
42[l]	1 : 3.6	15.03	48.98	35.99	2	Soft yellow + hard yellow.
46[l]	1 : 35	1.97	59.22	38.81	2	Hard yellow + 1 per cent. soft yellow.
48[l]	—	—	60.86	39.14	2	Hard yellow = FeS 1.120.

[a] At same heating.
[b] Cu : Fe of analysis shows Fe probably 0.2 per cent. low.

Table 10.—At 58 mm. between 4 : 1 and 1 : 2 (and probably from 1 : 0 to 0 : 1) 12-hour heatings at 900° were ample; even 6-hour heatings at 850° and 800° for 1 : 1 and 1 : 2 were satisfactory, but not at 750°. Absorption of sulphur by the charge while withdrawing the sulphur bulb from the furnace (see Tables 16–18) was not evident at 58 mm. The compositions of Table 10 are closely isothermal (Table 17*A*). From Table 12 and some unrecorded analyses of chalcopyrite at 750°, 800° and 850° it appears that the compositions at 1 : 1 and 1 : 2 are substantially the same at 775°, 58 mm. and 850°, 455 mm.

TABLE 10*A*. DISSOCIATION PRESSURES OF COVELLITE AND PYRITE ACCORDING TO ALLEN AND LOMBARD, RECALCULATED.[1]

Covellite. $2\,CuS \rightleftarrows S + Cu_2S_{1+}$.		Pyrite.[2] $FeS_2 \rightleftarrows S + FeS_{1+}$.	
Temp. ° C.	Pressure mm. Hg.	Temp. ° C.	Pressure mm. Hg.
400	1.4	575	0.8
410	2.5	595	4.4
433.7	12.+	610	14.
450	32.	625	39.
460	65.	635	72.
468	115.	645	130.
475	200.	655	198.
482	320.	665	263.
485	393.	672	343.
490	515.	680	520.
497	760.[a]	693	760.[a]

[a] Extrapolated.

[1] Pressures are read from plots, using the recent measurements of the vapor pressure of sulphur by W. A. West and A. W. C. Menzies, J. Phys. Chem., vol. 33, 1880. 1929.

[2] For chart of later measurements by other methods see R. Juza and K. Biltz, Das Zustandsdiagramm Pyrit, Magnetkies, Troilit und Schwefeldampf, beurteilt nach Schwefeldampfdrucken, Röntgenbildern, Dichten und magnetischen Messungen. Z. anorg. Chem., vol. 205, 273–86, 1932.

TABLE 11. STABILITY OF CHALCOPYRITE SOLID SOLUTION, $CuFeS_{1.94}$.

Temp. ° C.	Pressure mm.	Temp. ° C.	Pressure mm.
627	610	597	150
620	455	575	58
619	400	560	25
606	250	547	10–16

Table 11.—Temperatures were found by interpolation at which natural chalcopyrite acquired the above composition and was homogeneous. Slight corrections were made as for cubanite (Table 12) when the Cu to Fe ratio was not quite 1 : 1.

TABLE 12. DATA FOR DETERMINING THE TEMPERATURE OF STABILITY OF $CuFe_2S_3$ (CUBANITE) WHEN HEATED IN SULPHUR VAPOR.

Matte Used.	Sulphur Pressure mm.	Temp. °C.	Composition Wt. %. Cu.	Fe.	S.	Molal Ratio. Cu : Fe : S.	Adjusted Molal Ratio. Cu : Fe : S.	Remarks.
		850	23.34	41.31	35.35 [a]	0.9929 2 2.981	1 2 2.985	Soft yellow + a little hard yellow.
		790	23.23	41.29	35.48	0.9886 2 2.993	1 2 3.000	Soft yellow + trace hard yellow.
No. 67	760	779	23.19	41.10	35.71	0.9908 2 3.026	1 2 3.031	Soft yellow + some hard yellow.
		750	23.21	41.04	35.75	0.9936 2 3.033	1 2 3.036	Soft yellow + some hard yellow.
		730	23.08	41.00	35.92	0.9892 2 3.052	1 2 3.058	Soft yellow + trace hard yellow.
		850	23.44	41.45	35.11 [b]	0.9936 2 2.951	1 2 2.954	Soft yellow + few per cent. hard yellow.
		775	23.23	41.36	35.41	0.9867 2 2.983	1 2 2.990	Soft yellow + a little hard yellow.
		750	23.19	41.31	35.50	0.9863 2 2.994	1 2 3.001	Soft yellow + trace hard yellow.
No. 67	455	750	23.22	41.18	35.60	0.9905 2 3.011	1 2 3.016	Soft yellow + a few per cent. hard yellow.
		740	23.26	41.11	35.63	0.9940 2 3.019	1 2 3.022	Soft yellow + a little hard yellow.
		725	23.15	40.96	35.89 [c]	0.9929 2 3.051	1 2 3.055	Soft yellow + a little hard yellow.
		690	23.24	41.03	35.73 [d]	0.9947 2 3.032	1 2 3.035	Soft yellow + a little hard yellow.
No. 67		850	23.80	41.73	34.47	1.002 2 2.877	1 2 2.876	Soft yellow + hard yellow.
$CuFe_2S_3$		800	22.48	42.17	35.35	0.9365 2 2.919	1 2 2.953	Soft yellow + mere trace hard yellow.
$CuFe_2S_3$	58	800	22.63	42.44	34.93	0.9367 2 2.866	1 2 2.900	Soft yellow + trace hard yellow.
No. 67		800	23.41	41.69	34.90	0.9863 2 2.917	1 2 2.924	Soft yellow + some hard yellow.
No. 67		800	23.67	41.67	34.66	0.9979 2 2.899	1 2 2.900	Soft yellow + occasional trace hard yellow.
			Average value at 800°—58 mm. 2.923.					
$CuFe_2S_3$			23.01	41.40	35.59 [a]	0.9766 2 2.994	1 2 3.008	Soft yellow + trace hard yellow.
No. 67	58	750	23.61	41.21	35.18	1.006 2 2.972	1 2 2.969	Soft yellow + hard yellow.
No. 67			23.47	41.21	35.32	1.001 2 2.985	1 2 2.984	Soft yellow + a little hard yellow.
			Average value at 750°—58 mm. 2.988.					

[a] Sulphur *ca.* 0.1 per cent. high. [b] See also Table 17. [c] Sulphur *ca.* 0.2 per cent. high. [d] See Table 19.

Table 1.
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Table 12.—Figure 2 explains the presence of pyrrhotite at temperatures both higher and lower than equilibrium for ratios of Cu to Fe near 1 : 2. Along the isotherms near $CuFe_2S_3$, one per cent. increase in sulphur corresponds to about 4 per cent. of copper. Therefore, by translation along an isotherm, a ratio slightly different from 1 : 2 can be used to determine the sulphur content proper for the 1 : 2 ratio. Or, the molal ratios may be "adjusted" for Fe = 2, by changing the sulphur ratio 0.54 as much as is needed to make Cu = 1. If the adjusted ratios for sulphur are plotted against temperature, then at each pressure a temperature near which $CuFe_2S_3$ is stable can be found. At 800° a change of pressure from 58 mm. to 760 mm. increases sulphur 0.6–0.8 per cent.; and at all pressures between 58 mm. and 760 mm. lowering the temperature from 850° to 750° increases sulphur 0.5–0.6 per cent.

[a] Sulphur *ca.* 0.1 per cent. high. [b] See also Table 17. [c] Sulphur *ca.* 0.2 per cent. high. [d] See Table 19.

Average value at 750°—58 mm. 2.988.

TABLE 13. DATA FOR DETERMINING THE TEMPERATURE OF STABILITY OF Cu_5FeS_4 IN SULPHUR VAPOR.
(See Tables 17, 21, 24.)

Matte Used No.	Sulphur Pressure mm.	Temp. ° C.	Composition Wt. %. Cu.	Fe.	S.	Molal Ratio. Cu : Fe : S.	Adjusted Molal Ratio. Cu : Fe : S.	Remarks.
60		820	63.57	11.12	25.31	5.025 : 1 : 3.966	5 : 1 : 3.953	
60		790	63.51	11.03	25.46	5.056 : 1 : 4.020	5 : 1 : 3.990	Homogeneous orange.
60		790	63.60	11.01	25.39	5.073 : 1 : 4.016	5 : 1 : 3.976	
59		779	63.22	11.16	25.62	4.975 : 1 : 3.997	5 : 1 : 4.011	Orange + trace soft yellow.
60		779	63.42	11.03	25.55	5.051 : 1 : 4.035	5 : 1 : 4.007	
60	760	750	63.55	10.94	25.51	5.102 : 1 : 4.063	5 : 1 : 4.008	Homogeneous orange.
60		740	63.40	10.93	25.67	5.093 : 1 : 4.088	5 : 1 : 4.038	
60		730	63.36	10.94	25.70	5.090 : 1 : 4.094	5 : 1 : 4.045	
60		540	62.91	10.99	26.10	5.028 : 1 : 4.136	5 : 1 : 4.121	Orange + a little soft yellow.
60		500	63.13	10.86	26.01	5.104 : 1 : 4.171	5 : 1 : 4.115	Orange + 10 per cent. soft yellow.
60		850	63.75	11.12	25.13	5.034 : 1 : 3.934	5 : 1 : 3.918	
60		850	63.76	11.03	25.21	5.079 : 1 : 3.982	5 : 1 : 3.939	Homogeneous orange.
60		750	63.53	11.01	25.46	5.071 : 1 : 4.025	5 : 1 : 3.987	
60		740	63.47	11.05	25.48	5.044 : 1 : 4.016	5 : 1 : 3.992	
60	455	725	63.27	11.02	25.71	5.043 : 1 : 4.059	5 : 1 : 4.036	
60		700	63.14	11.02	25.84	5.033 : 1 : 4.085	5 : 1 : 4.067	Orange + soft yellow.
60		612	63.17	11.01	25.82	5.048 : 1 : 4.086	5 : 1 : 4.060	
59		612	62.89	11.11	26.00	4.974 : 1 : 4.077	5 : 1 : 4.091	

Table 13.—No other solid solution of the system changes sulphur content so slowly with change of temperature as the chalcocite solid solution near 5 : 1. Ordinary experimental errors may cause analyses to overlap for preparations 100° apart. Molal ratios have been adjusted on the same basis as in Table 12.

The composition Cu_4FeS_4 is within the area of chalcocite solid solution. Compositions in this vicinity unmix at irregular rates during cooling, those richer in sulphur and iron have been described under Table 8.

Judging from pictures and descriptions, the intergrowth patterns in natural bornite are in three directions the same as in these chalcocite solid solutions (Note, discussion Table 14). However, by Geijer* and some writers to whom he refers, the lamellæ of chalcopyrite are said to follow octahedral cleavage in the bornite. This would require lamellæ in four directions. Geijer's (p. 31) "orange-colored bornite" which contains chalcopyrite lamellæ in "octahedral" pattern is probably not like the "orange bornite" of Murdock.[3] (See p. 229.)

* Per Geijer, Some Swedish Occurrences of Bornite and Chalcocite, Sveriges Geol. Undersokn., Arsbok, vol. 17, No. 2 (1923), pp. 6, 8, 14, 18, 31, and especially 41; and Fig. 12.

TABLE 14. COMPOSITIONS OF CHALCOCITES AT VARIOUS TEMPERATURES AND PRESSURES.[1]

Temp. ° C.	Sulphur press. mm.	Extrapolated Comp. Wt. %.[a] Cu.	S.	S : 2 Cu (Molal).	Exper. Comp. Wt. %. Cu.	S.	S : 2 Cu (Molal).
1130	(H_2S)[1]	—	—	—	79.16	20.84	1.044
1170	(H_2S)	79.2	20.8	1.042	79.20	20.80	1.042
900	2	78.9	21.1	1.060	79.14	20.86	1.045
850	455	78.5	21.5	1.086	78.60	21.40	1.080
850	455	—	—	—	78.42	21.58	1.092
750	455	78.2	21.8	1.106	78.13	21.87	1.110
667	455	78.0	22.0	1.118	77.88	22.12	1.126
602	455	77.75	22.25	1.135	77.67	22.33	1.140
540	455	—	—	—	77.85	22.15	1.128
490	455	77.5	22.5	1.15	—	—	—
540	760	—	—	—	77.51	22.49	1.151
500	760	77.5	22.5	1.15	77.69	22.31	1.139

[1] See Ref. 21 for compositions in H_2S at lower temperatures; see Table 45.
[a] Obtained by extrapolation from iron-bearing chalcocites.

Table 14.—Data for the extrapolated compositions appear in succeeding tables. At 455 mm. the increase in sulphur in the chalcocite solid solutions appears linear with respect to decreasing temperature. At other pressures data are fragmentary, except that for hydrogen sulphide (Ref. 21) as well as at 455 mm., at 50° above the temperature at which covellite changes to chalcocite, the chalcocite has closely the composition $Cu_2S_{1.15}$ (Cu 77.5, S 22.5 per cent.). Along its dissociation pressure curve covellite changes to chalcocite containing slightly more sulphur (probably not as much as 23.0 per cent. at any temperature between 360° and 500°, but analyses of some natural chalcocite * have indicated as much as 24.5 per cent.).

* W. Kurz, Z. Krist., vol. 92, 408, 1935. Discusses relation of intergrowths to crystal structure of chalcopyrite, covellite, chalcocite and bornite, although structure data on the last are meager.

TABLE 15. EXTRAPOLATED AND EXPERIMENTALLY DETERMINED COMPOSITIONS OF PYRRHOTITES.

Temp. ° C.	Sulphur press. mm.	Extrapolated Comp. Wt. %.[a] Fe.	S.	S : Fe (Molal).	Experimental Comp. Wt. %. Fe.	S.	S : Fe (Molal).	Magnetic Properties.
677	455	—	—	—	59.58	40.42	1.18	
690	455	59.5	40.5[b]	1.19	—	—	—	
750	455	59.6	40.4	1.18	59.77	40.23	1.172	
750	455	—	—	—	59.51	40.49	1.185	Strongly
780	760	—	—	—	59.85	40.15	1.168	magnetic
850	455	60.0	40.0	1.16	60.02	39.98	1.163	
850	455	—	—	—	60.19	39.81	1.152	
900	58	60.8	39.2	1.12	60.86	39.14	1.120	
1250	(H_2S)	61.9	38.1	1.07	61.69	38.31	1.082	
1170	(H_2S)	—	—	—	61.93	38.07	1.071	
1230	(H_2S)	—	—	—	62.51	37.49	1.049	Slightly
1200	(H_2S)	—	—	—	62.94	37.06	1.026	magnetic
1250	Melted in evacuated tubes				62.70	37.30	1.036	
1250	Melted in evacuated tubes				63.48	36.52	1.002	

[a] Obtained in part by extrapolation from copper-bearing pyrrhotites.
[b] Corrected for pyrite.

TABLE 16. HEATINGS AT 900° (AND 950°*), 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 18).
60	5 : 1*	63.90	11.09	25.01	1	Mottled gray and orange.
22	2 : 1	49.96	21.46	28.57	2	Orange + soft yellow + trace metallic Cu.
65[h]	2⅛ : 1	50.62	20.84	28.54	2	Orange + soft yellow + trace metallic Cu.
27	1 : 1	36.20	31.60	32.20	2	Homogeneous, soft yellow.
($CuFeS_2$[h])	1 : 1	36.06	31.91	32.03	2	Homogeneous, soft yellow.

TABLE 17. ISOTHERM 850°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 18).
2	—	78.60	—	21.40	2	Originally mottled gray. Now homogeneous, gray $Cu_5S_{1.080}$.
(CuS[h])	—	78.42	—	21.58	2	Homogeneous, gray $Cu_2S_{1.092}$.
52[h]	17 : 1	73.64	3.67	22.69	2	Homogeneous, gray.
5	16.3 : 1	73.23	3.99	22.78	2	Homogeneous, gray.
6	11 : 1	70.75	5.78	23.47	1	Homogeneous, gray.
55[h]	7 : 1	66.86	8.57	24.57	1	Homogeneous, gray.
57	6 : 1	65.67	9.65	24.68	1	Homogeneous, orange-gray.
60	5 : 1	63.75	11.12	25.13	1	Homogeneous, orange-gray.
61[h]	5 : 1	63.39	11.17	25.44	2	Homogeneous, orange-gray.
63	4 : 1	60.85	13.21	25.94	2	Homogeneous, orange-gray.
74[h]	4 : 1	60.55	13.18	26.27	2	Orange-gray + traces of soft yellow.
16	4 : 1	60.67	13.22	26.11	2	Orange-gray + traces of soft yellow.
64[h]	3 : 1	56.25	16.58	27.17	2	Orange-gray + soft yellow coarse grains, coarse and fine gashes.
65*A*	2 : 1	49.33	21.76	28.91	2	Orange-gray + soft yellow.
65[h]	2⅛ : 1	50.51	20.88	28.61	2	
23	1⅔ : 1	46.04	24.10	29.86	2	Interstitial and reticulate orange-gray in soft yellow.
24	1.5 : 1	43.84	25.76	30.40	2	Orange-gray + soft yellow.
25	1.3 : 1	41.38	27.66	30.96	2	Soft yellow + orange-gray.
26	1.09 : 1	37.72	30.35	31.93	2	Soft yellow, homogeneous.
27	1 : 1	36.17	31.29	32.54	2	Soft yellow, homogeneous.
($CuFeS_2$[h])	1 : 1	35.76	31.68	32.56	1	Soft yellow, homogeneous.
68	1 : 2	23.49	41.52	34.99	1	Soft yellow + a little hard yellow.
37	1 : 2¼	21.63	42.81	35.56	2	Soft yellow + hard yellow.
39	1 : 2.6	19.50	44.58	35.92	2	Soft yellow + hard yellow.
41	1 : 3.2	16.57	46.76	36.67	2	Soft yellow + hard yellow.
42	1 : 3.6	14.81	48.22	36.97	2	Soft yellow + hard yellow.
71	1 : 5	11.74	50.65	37.60	2	Hard yellow + soft yellow.
45	1 : 19	3.49	57.27	39.23	1	Hard yellow + soft yellow.[k]
46	1 : 35	1.95	58.67	39.38	2	Hard yellow + trace of soft yellow.
48	—	—	60.02	39.98	2	Originally $FeS_{1.023}$. Now $FeS_{1.163}$. Homogeneous, hard yellow.

[h] Sulphur before heating higher than in the equilibrium products.
[k] Serrate outlines, probably from slight unmixing.

TABLE 17A. COORDINATES FOR ISOTHERMS.[a]

	Chalcocite s.s.	5 : 1.	M–F.	N–K.	1 : .1	Q– (or L–) $CuFe_2S_3$.	Pyrrhotite s.s.
			750°–455 mm.				
Fe	—	(11.1)	(14.9)	23.6	31.2	40.0	59.6
S	(21.9)	(25.5)	(27.0)	30.5	33.2	35.4	40.4
			850°–455 mm.				
Fe	—	11.2	15.8	26.0	31.5	40.6	60.0+
S	21.5	25.3	26.9	30.5	32.5	35.0	40.0−
			900°–58 mm.				
Fe	—	11.2	16.6	28.6	32.0	38.6	60.8
S	(21.2)	25.0	26.9	30.5	31.5	33.3	39.2
			H_2S.[b]				
Fe	—	11.3	18.6	—	32.3	37.5	61.7
S	20.7	24.5	26.9	—	30.9	32.3	38.3

[a] Others, Table 36A.
[b] See Table 5.

TABLE 18. ISOTHERM 750°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Table 1).
64	3 : 1	55.79	16.70	27.51[a]	1	Soft yellow with orange streaks + orange-gray with fine yellow gashes.
65A	2 : 1	48.89	21.49	29.62	1	Soft yellow + orange-gray gashes, equal amounts.
23	1⅔ : 1	45.38	23.89	30.73	2	Soft yellow + irregular network of orange-gray.
24	1.5 : 1	43.46	25.42	31.12	2	Soft yellow + irregular network of orange-gray.
25	1.3 : 1	40.87	27.32	31.81	2	Soft yellow + irregular network of orange-gray.
26	1.09 : 1	37.25	29.93	32.82	2	Soft yellow.
66	1 : 1	35.52	31.32	33.16	2	Soft yellow.
($CuFeS_2$[b])	1 : 1	35.37	31.38	33.25	2	Soft yellow.
37	1 : 2¼	21.58	42.47	35.95	2	Soft yellow + hard yellow.
39	1 : 2.6	19.34	44.26	36.40	2	Soft yellow + hard yellow.
41	1 : 3.2	16.50	46.54	36.96	2	Hard yellow + soft yellow.
48	—	—	59.51	40.49	2	Hard yellow = FeS 1.185.
FeS_2[b]	—	—	59.8	40.2[b]	1	Hard yellow = FeS 1.172.

[a] Sulphur probably low, included to show phases.
[b] Approximately.

Tables 16, 17, 17A and 18.—At 850° equilibrium was approached from both directions. Several chalcocite solid solutions heated at 900° or 950° had compositions like those at 850°. It was concluded that a slight absorption of sulphur took place during the removal of the bulbs from the furnace. Some of the compositions of products containing chalcocite solid solutions are tabulated to show their relation to phase compositions. By extrapolation along an isotherm (see 1½ : 1 and 1.09 : 1, Table 10) the chalcocite Cu 57., Fe 16.1, S 26.9 is richest in sulphur and iron in which metallic copper has been found; chalcocite compositions below (in sulphur) the melting boundary at 455 mm. have usually shown decided mottling.

TABLE 19. PARTIAL ISOTHERM 690°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 20).
$CuFeS_2$[k]	1 : 1	35.12	31.14	33.74	2	Soft yellow.
27	1 : 1	35.51	30.93	33.56	2	Soft yellow.
33	1 : 1⅓	30.06	35.30	34.64	2	Soft yellow.
34	1 : 1⅔	26.64	38.27	35.09	2	Soft yellow + traces hard yellow.
68	1 : 2	23.24	41.03	35.73	2	Soft yellow + a little hard yellow.
71	1 : 5	11.56	50.05	38.39	2	Hard yellow + soft yellow + a little py.
49	—	—	59.32	40.68	2	Originally FeS 1.071. Now FeS 1.19, *ca.* 1 per cent. superficial py.

TABLE 20. PARTIAL ISOTHERM 677°, 455 MM.

Matte * Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Table 1).
30(602°)	1 : 1.2	31.86	33.81	34.33	1	Soft yellow.
33(602°)	1 : 1⅓	30.06	35.28	34.66	1	Soft yellow.
34(602°)	1 : 1⅔	26.64	38.26	35.10	1	Soft yellow + a little hard yellow.
34(602°)	1 : 1⅔	26.49	38.30	35.21	1	Mostly soft yellow. Some hard yellow. Bare trace FeS_2.
34	1 : 1⅔	26.51	38.23	35.26 †	2	Soft yellow + hard yellow + trace superficial FeS_2.
34	1 : 1⅔	26.61	38.28	35.11	1	Soft yellow.
68(602°)	1 : 2[a]	23.03	40.94	36.03	1	Soft yellow + hard yellow, trace FeS_2.
68(602°)	1 : 2[b]	22.57	40.37	37.06	1	Soft yellow + a little hard yellow + FeS_2.
68	1 : 2[c]	22.61	40.20	37.19 †	2	Soft yellow + a little hard yellow + FeS_2.
68	1 : 2[d]	23.10	41.01	35.89	1	Soft yellow + a little hard yellow, no FeS_2.
71	1 : 5	10.72	45.76	43.52 †	2	Hard yellow + soft yellow + FeS_2.
48	—	—	59.58	40.42	2	Hard yellow only.
49	—	—	59.27	40.73	1	Hard yellow + a little FeS_2.

* Those marked (602°) contained before heating more sulphur than the equilibrium product.

† Three preparations at the same heating.

[a–d] See discussion of table.

Tables 19 and 20 (see Table 21).—According to Fig. 2 the indicated temperature difference, 13°, represents a barely detectable difference of 0.1 per cent. in sulphur. The observed differences are mostly less than this. Comparison of the two heatings at 690° with the one at 677° indicates substantially equilibrium for both, except that the differences in composition of the four 1 : 2 products may be explained by slight irregularities of temperature control, and the direction of approach toward a composition in which a reaction is concerned involving several per cent. of sulphur. Preparations *b* and *d* which were heated together represent either the reaction temperature or a slightly higher temperature; *a* represents a slightly higher, and *c* (with 1 : 5) a slightly lower temperature. The reaction is the formation of pyrite and cubanite (solid solution L) from pyrrhotite (solid solution J), and the inferred temperature is 675°.

TABLE 21. ISOTHERM 667°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 23).
1	∝ : 1	77.88	—	22.12	1	Homogeneous. Cu_2S 1.126.
12	6 : 1	65.21	9.63	25.16	2	Homogeneous, orange-gray.
14	5 : 1	63.42	10.92	25.66	2	Orange-gray + trace soft yellow gashes.
16	4 : 1	60.23	13.19	26.58	2	Orange-gray + soft yellow grains.
19	3 : 1	55.71	16.37	27.92	2	Orange-gray + soft yellow grains with reticulate orange.
23	1⅔ : 1	45.10	23.80	31.10	2	Soft yellow + orange-gray gashes.
24	1.5 : 1	43.01	25.25	31.74	2	Soft yellow + orange-gray gashes.
25	1⅓ : 1	40.54	27.15	32.31	2	Soft yellow + orange-gray gashes.
26	1.09 : 1	37.04	29.75	33.21	2	Soft yellow (trace of orange-gray).
27	1 : 1	35.31	30.97	33.72	2	Soft yellow, homogeneous.
$(CuFeS_2)^h$	1 : 1	35.17	31.04	33.79	2	Soft yellow, homogeneous.
30(602°) *	1 : 1.2	31.97	33.59	34.44	1	Soft yellow.
30	1 : 1.2	31.80	33.61	34.59	2	Soft yellow.
33(602°)	1 : 1⅓	29.92	34.95	35.13	1	Soft yellow (trace of residual (?) py.).
34(602°)	1 : 1⅔	25.55	36.72	37.73	1	Soft yellow, faint reticulate structure + py.
34	1 : 1⅔	26.36	37.84	35.80	2	Soft yellow, faint reticulate structure + py.
36(602°)	1 : 2	21.53	38.19	40.28	1	Soft yellow + pyrite.
68	1 : 2	23.05	40.91	36.04	1	Soft yellow + hard yellow (trace py.).
70	1 : 4	12.83	49.02	38.15	1	Soft yellow + hard yellow.
71	1 : 5	11.01	47.63	41.36	1	Soft yellow + hard yellow + pyrite.
48	1 : ∝	—	57.16	42.84	1	Hard yellow + pyrite.
FeS_2	1 : ∝	—	—	—	1	Pyrite unchanged.

* See Table 20.

Tables 19, 20 and 21 (see Table 20).—At temperatures above 680° and pressures below 455 mm. isotherms are nearly parallel across the whole diagram Fig. 2. They traverse the three fields of solid solution and the intervening fields. Just below 680° the pressure 455 mm. is sufficiently high to cause pyrrhotite solid solutions to absorb and react with sulphur to form pyrite, FeS_2, whereby the compositions change in that direction. Under the conditions of heating in order to make the changes take place in a few hours the temperatures must be over-stepped several degrees. The most complex reaction here is the change at 675° of the copper-rich pyrrhotite, J, into pyrite and a member of the intermediate solid solution series. At this temperature the compositions of these three phases form the corners of a triangular isothermal field. That the temperature of this field is above 667° is shown by preparations 1 : 5 and 1 : 1⅔ (No. 34) of Table 21, and that it is above that of one of the heatings recorded as 677° is shown by 1 : 5 and 1 : 2 (No. 68) of Table 20. However, it is below the temperature of two other such heatings, both 1 : 2 [No. 68 (602)]. From these data the value 675° ± 5° is inferred.

Most of the compositions of Tables 20 and 21 at 677° and 667° are too scattered and far from equilibrium to establish the composition of the intermediate solid solution, but the 675° isotherm of Fig. 2 may be traced from near the center of the intermediate solid solution area toward cubanite where it crosses the boundary at L. This is the desired composition. Several compositions at ratios of 1 : 1⅔ and 1 : 2 are close to the boundary. Three of them do not contain pyrite. At the boundary the inferred composition, L, is Cu 25.4, Fe 39.2, S 35.4. That this composition is correct is shown by the microscopical analysis. 1 : 2, Table 21.

The line L–FeS_2 (Fig. 2) is the highest of a series of isotherms radiating from FeS_2 to the intermediate ternary solid solutions. At temperatures near the isothermal reaction fields the attainment of equilibrium is, in general, not realized, but if the reaction products exhibit clear microscopical differences the broader relationships may be inferred.

During the few minutes charges rich in pyrrhotite have been coming to temperature, grains often acquired a protective coating of pyrite. Scattered little nodules of pyrite, present in some preparations which otherwise conform to conditions in the solid solution fields, appear to have formed similarly.

Between 675° and 637° some details are in doubt. The possibility remains that solid solution between $CuFe_2S_3$ and the rest of the intermediate solid solution may be interrupted, with a break in the low-temperature boundary. If interruption exists at all temperatures a field such as M-N-K-F would intervene; if only lower temperatures are involved, then a cup-shaped depression would appear in the boundary of the intermediate solid solution with an isotherm *ca.* 660° across the top, and higher isotherms nearly parallel to it. In either case a narrow isothermal field extending from FeS_2 to the break in the boundary would come in between the 650° and 675° isotherms.

TABLE 22. PARTIAL ISOTHERM 637°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 28).
$CuFeS_2$	1 : 1	34.91	31.07	34.02	2	Soft yellow (trace of orange-gray).
30 (602°) *	1 : 1.2	31.75	33.40	34.85	2	Soft yellow (trace of pyrite).
33 (602°)	1 : 1⅓	29.45	34.58	35.97	2	Soft yellow + a little pyrite.
34 (602°)	1 : 1⅔	25.21	36.38	38.41	2	Soft yellow + pyrite.
68 (602°)	1 : 2	21.17	37.97	40.86	2	Soft yellow + much pyrite.

* See Table 20.

TABLE 23. PARTIAL ISOTHERM 620°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 28).
66	1 : 1	34.85	30.96	34.19	2	Soft yellow.
30 (602°) *	1 : 1.2	31.15	32.95	35.90	1	Soft yellow + py.
33 (602°)	1 : 1⅓	28.99	33.96	37.05	1	Soft yellow + py.
34 (602°)	1 : 1⅔	24.86	35.92	39.22	1	Soft yellow + py.
68 (602°)	1 : 2	20.98	37.40	41.62	1	Soft yellow + py.
?	1 : 2	20.32	37.75	41.93	2	Soft yellow + py.

* See Table 20.

TABLE 24. DATA FOR INTERPOLATING THE ISOTHERM 602°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Temp. ° C.	Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 28).
1	∝ : 1	605	77.67	—	22.33	1	Gray, homogeneous, Cu_2S 1.140.
4	29 : 1	605	74.77	2.28	22.95	1	Gray, homogeneous.
52	17 : 1	605	72.94	3.57	23.49 *	1	Gray, homogeneous.
53	14 : 1	605	71.75	4.50	23.75 *	1	Gray, homogeneous.
54	9 : 1	605	68.66	6.77	24.57 *	1	Gray, homogeneous.
55	7 : 1	605	66.46	8.48	25.06 *	1	Grayish orange, homogeneous.
14	5 : 1	602	63.34	10.86	25.80	3	Grayish orange + some soft yellow.
16	4 : 1	602	60.15	13.09	26.76	3	Grayish orange + soft yellow.
19	3 : 1	602	55.54	16.28	28.18	3	Grayish orange + soft yellow.
65	2⅛ : 1	600	49.48	20.50	30.02	1	Grayish orange + soft yellow.
65A	2 : 1	605	48.29	21.28	30.43	2	Grayish orange unmixed from soft yellow. No py.
22	2 : 1	602	48.76	21.02	30.22	3	Grayish orange + soft yellow.
23 (460°) [a]	1⅔ : 1	602	44.94	23.72	31.34	3	Soft yellow + grayish orange, no py.
23	1⅔ : 1	602	44.98	23.68	31.34	3	Soft yellow + grayish orange.
24	1.5 : 1	602	42.89	25.08	32.03	3	Soft yellow + grayish orange.
25 (460°)	1⅜ : 1	602	40.67	26.69	32.64	3	Soft yellow + trace grayish orange + a little py.
25	1⅜ : 1	602	40.15	26.88	32.97	3	Soft yellow + several per cent. grayish orange (unmixed).
26	1.09 : 1	602	36.67	29.63	33.70	2	Soft yellow only.
26	1.09 : 1	602	36.68	29.51	33.81	3	Soft yellow (trace of orange).
26	1.09 : 1	602	36.65	29.46	33.89	3	Soft yellow (trace of orange + py.).

TABLE 24 (*Continued*).

Matte Used.	Cu : Fe (Molal).	Temp. °C.	Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 28).
66	1 : 1	600	34.49	30.56	34.95	2	Soft yellow (trace of pyrite).
66	1 : 1	610	34.87	30.77	34.36	2	Soft yellow, homogeneous.
66	1 : 1	605	34.78	30.72	34.50	2	Soft yellow (trace of py.).
66	1 : 1	600	34.50	30.52	34.98	2	Soft yellow (trace of orange + py.).
($CuFeS_2$)	1 : 1	590	34.25	30.27	35.48	2	Soft yellow + some py. and orange.
do. (460°)	1 : 1	602	34.50	30.65	34.85	3	Soft yellow + pyrite.
do. (460°)	1 : 1	602	34.64	30.64	34.72	3	Soft yellow + pyrite.
66	1 : 1	602	34.55	30.70	34.75	2	Soft yellow (trace py. + orange).
27	1 : 1	602	34.87	30.55	34.58	2	Soft yellow (trace py.).
27	1 : 1	602	35.05	30.61	34.34	2	Soft yellow (trace py.).
27	1 : 1	602	34.77	30.45	34.78	3	Soft yellow + considerable py. + orange.
30	1 : 1.2	602	30.72	32.41	36.87	2	Soft yellow + pyrite.
30	1 : 1.2	602	30.68	32.34	36.98	3	Soft yellow + pyrite.
33	1 : 1⅓	602	28.44	33.46	38.10	2	Soft yellow + pyrite.
32 (460°)*	1 : 1⅓	602	28.87	33.37	37.76	3	Soft yellow + pyrite.
32 (460°)	1 : 1⅓	602	28.98	33.26	37.76	3	Soft yellow + pyrite.
34	1 : 1⅔	602	24.68	35.38	39.94	2	Soft yellow + pyrite.
36	1 : 2	602	21.04	36.78	42.18	3	Soft yellow + pyrite.
36 (460°)	1 : 2	602	21.08	37.03	41.89	3	Soft yellow + pyrite.
69	1 : 3	602	14.97	39.68	45.35	2	Soft yellow + pyrite.
70	1 : 4	602	11.17	41.64	47.19	2	Soft yellow + pyrite.

* One heating adequate, mattes have about same composition as products.
[a] High sulphur from heating at 460°, 455 mm.

Table 24.—The 1 : 1 mattes absorb sulphur readily up to 34.4 per cent. and remain homogeneous. Further absorption is attended by a variable lag, and the formation of pyrite. 620° is the observed equilibrium for this composition; and at 602° for the composition of ordinary chalcopyrite (34.95 per cent. S), which composition represents here considerable pyrite, and was not quite reached after heating 12 hours.

TABLE 25. ISOTHERM 580°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 28).
14	5 : 1	63.36	10.86	25.78	3	Orange + some soft yellow, no py.
16	4 : 1	60.19	13.07	26.74	3	Orange + some soft yellow grains, no py.
19	3 : 1	55.58	16.17	28.25	3	Orange + grains of soft yellow with reticulate orange, no py.
22	2 : 1	48.70	21.08	30.22	3	Orange + soft yellow, no py.
23	1⅔ : 1	44.88	23.54	31.58	3	Orange + soft yellow, no py.
23[h]	1⅔ : 1	44.96	23.59	31.45	3	Orange + soft yellow, no py.
24	1.5 : 1	42.83	24.94	32.23	3	Soft yellow with reticulate orange, no py.
25	1⅓ : 1	40.28	26.87	32.85	3	Soft yellow + orange + distinct py.
25[h]	1⅓ : 1	40.46	26.66	32.88	3	Soft yellow + orange + distinct py.
26	1.09 : 1	35.96	28.97	35.07	3	Soft yellow + some orange + py.
27	1 : 1	34.17	29.91	35.92	3	Soft yellow + some orange + py.
($CuFeS_2$)	1 : 1	34.04	30.06	35.90	3	Soft yellow + some orange + py.
($CuFeS_2$[h])	1 : 1	33.79	30.10	36.11	3	Soft yellow + some orange + py.
32	1 : 1⅓	28.31	32.89	38.80	3	Soft yellow + some orange + py.
32[h]	1 : 1⅓	28.56	32.80	38.64	3	Soft yellow + some orange + py.
67	1 : 2	20.91	36.75	42.34	1	Soft yellow + some orange + py.
36[h]	1 : 2	20.86	36.56	42.58	3	Soft yellow + some orange + py.

[h] See discussion Table 21. (Preheated.)

TABLE 26. ISOTHERM 560°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 28).
14	5 : 1	63.37	10.83	25.80	3	Orange + soft yellow, no py.
16	4 : 1	60.13	13.04	26.83	3	Orange + soft yellow in unmixed granules, and films.
19	3 : 1	55.58	16.20	28.22	3	Orange + soft yellow, no pyrite.
22	2 : 1	48.54	21.00	30.46	3	Soft yellow with interstitial and reticulate orange + py.
23	1⅔ : 1	44.6	23.4	32.0[a]	3	Orange in soft yellow pattern + considerable py.
23[h]	1⅔ : 1	44.15	23.16	32.69	3	
24	1.5 : 1	42.56	24.75	32.69	3	
25	1⅓ : 1	39.42	26.24	34.34[a]	3	
26	1.09 : 1	35.38	28.50	36.12	3	
27	1 : 1	33.34	29.45	37.21	3	Soft yellow + reticulate orange + py.
($CuFeS_2$)	1 : 1	33.50	29.44	37.06	3	
($CuFeS_2$[h])	1 : 1	33.27	29.41	37.32	3	
32	1 : 1⅓	28.07	32.40	39.53	3	
32[h]	1 : 1⅓	28.20	32.23	39.56	3	
36[h]	1 : 2	20.60	36.16	43.24	3	

[h] See discussion Table 21.
[a] See discussion Table 28.

TABLE 27. PARTIAL ISOTHERM 550°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 28).
19	3 : 1	55.32	16.17	28.51	3	Orange + soft yellow grains + some py.
22	2 : 1	48.12	20.80	31.08	3	Orange + soft yellow + some py.
23	1⅔ : 1	44.19	23.30	32.51	3	Orange + soft yellow + py.
24	1.5 : 1	42.13	24.61	33.26	3	Soft yellow + orange + py.
26	1.09 : 1	34.99	27.99	37.02	3	Soft yellow + granular and reticulate orange + py.
($CuFeS_2$)	1 : 1	33.09	29.24	37.67	2	Soft yellow + orange + py.
($CuFeS_2$)[h]	1 : 1	33.00	29.20	37.80	2	Soft yellow + orange + py.
32	1 : 1⅛	27.47	31.83	40.70	3	Soft yellow + much interstitial and granular orange + py.

[h] See discussion Table 21.

Table 27.—($CuFeS_2$)[h] originally high in sulphur contained pyrite and chalcocite solid solution. During heating sulphur was evolved and the reaction formed chalcopyrite (intermediate) solid solution, N. During cooling this unmixed and regenerated lamellæ of chalcocite solid solution, therefore, the temperature of this heating was surely above the equilibrium temperature: Pyrite + chalcocite s.s. $\rightleftarrows$ intermediate (chalcopyrite) s.s. + sulphur. The $CuFeS_2$ heated at the same time came to almost the same composition by absorbing sulphur, at a temperature which could have been either above or slightly below the equilibrium temperature. Three other charges—mattes 26 and 32 and $CuFeS_2$—that contained no granular chalcocite solid solution before heating, developed it while heating, thus reversing the reaction observed in ($CuFeS_2$).[h] The slight difference in temperature necessary to cause the reversal of the reaction is probably less than 5°, and the equilibrium temperature here is 550°. This is, therefore, the temperature of an isothermal field. (See discussion, Table 28.)

The intermediate solid solutions formed at 550° with compositions near N (Fig. 2) recrystallize completely (invert and unmix) at some temperature range not above 550° (Table 27). During cooling, when inversion starts, new lamellæ grow within the old phase parallel to its crystallographic planes (probably rhombohedral, Table 8) and form a fairly uniform meshwork of nearly pure chalcopyrite. The chalcocite which had been in solution in the old phase is thus concentrated in the interstices of the meshwork, particularly in a film around the lamellæ. Thus a constriction appears where one lamella grows against another. (A criterion which has been used as proof of unmixing.) As recrystallization progresses the interstices become filled with a fine grid-like mixture of the inverted phase and the exsolved phase.

The grid texture is present in even the small amounts of chalcocite solid solution that segregate from compositions near $CuFeS_2$.

For textures in the compositions near M (Fig. 2) see Table 8.

TABLE 28. ISOTHERM 540°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Table 1).
1	—	77.85	—	22.15 *	3	Homogeneous, gray.
60	5 : 1	63.08	10.93	25.99 *	3	Orange + *ca.* 4 per cent. soft yellow, no py.
14	5 : 1	63.34	10.89	25.77	3	Orange + soft yellow variable, no py.
16	4 : 1	60.07	13.07	26.86	3	Orange + *ca.* 20 per cent. soft yellow grains, no py.
		60.11	13.05	26.84 *	3	
64	3 : 1	55.05	16.38	28.57 *	3	Orange + soft yellow, distinct py.
19	3 : 1	55.49	16.27	28.24	3	Orange + soft yellow, distinct py.
22	2 : 1	48.27	20.89	30.84	3	
22	2 : 1	47.89	20.76	31.35	3	
23	1⅔ : 1	44.22	23.21	32.57	3	
23 [h]	1⅔ : 1	42.90	22.53	34.57	3	
23	1⅔ : 1	43.94	23.06	33.00	3	
24	1.5 : 1	41.55	23.73	34.72	3	
25	1½ : 1	38.10	25.33	36.57	3	
25 [h]	1½ : 1	38.10	25.37	36.53	3	Orange + little soft yellow + py.
26	1.09 : 1	34.41	27.43	38.16	3	
27	1 : 1	32.68	28.31	39.01	3	
($CuFeS_2$)	1 : 1	32.24	28.58	39.18	3	
($CuFeS_2$) [h]	1 : 1	32.30	28.55	39.15	3	
32	1 : 1½	27.05	31.49	41.46	3	
32 [h]	1 : 1½	27.38	31.38	41.24	3	
68	1 : 2	19.98	35.36	44.66 *	3	
36 [h]	1 : 2	20.11	35.31	44.58	3	

[h] See discussion Table 21; preheated at 460°—455 mm.
* All at one heating.

Table 28 (and Tables 24–27).—The compositions at 560° and 540° containing more iron than 1½ : 1 lie regularly along lines radiating from FeS_2, but for several higher copper to iron ratios irregularities are evident. In the former at 560° the phases are pyrite, and intermediate solid solution, which has unmixed, probably during inversion, so as to produce an intricate reticulate orange and yellow texture; at 540° the phases are pyrite and chalcocite solid solution and the latter has scattered gashes of unmixed intermediate solid solution. Therefore a phase change (reaction) takes place at some intermediate temperature. Correspondingly, the spacing of the isotherms 540°–560° is too wide to be in accord with those at higher and lower temperatures. The interposition of the isothermal reaction field at 550° (Table 27) accounts for these conditions. In this field pyrite and chalcocite solid solution (M, Fig. 2) are in equilibrium. The time required for the attainment of equilibrium in our charges where two or more of these phases were concerned, was variable. If pyrite was absent originally, its formation and growth lagged progressively more as copper to iron increased. After heating for 18 hours such preparations as 1⅔ : 1, 2 : 1, and 3 : 1 at 540°, and 4 : 1 at 520° contained only about half the required amount of pyrite; on the other hand 1⅔ : 1 and 1½ : 1 at 560° absorbed slightly more sulphur than the general trend of the isotherms represents. The following explanation is offered. Originally these preparations were mattes containing a mixture of relatively coarse grains of chalcocite solid solution, near 2⅔ : 1, and intermediate solid solution, near 1⅛ : 1. During heating some more isolated grains of each would absorb sulphur without reacting correspondingly with each other. They would soon closely approach points on the 560° isotherm at these ratios of Cu to Fe. The average sulphur content at 1⅔ : 1 on a straight line between these points is

decidedly above the equilibrium sulphur content for uniform grains of 1⅔ : 1. The grains of 2½ : 1 should contain no pyrite, in those of 1⅕ : 1 pyrite should be abundant. Microscopical observations accord with this explanation.

From Tables 23–32 and observations included here, the Fe and S coordinates of the following points (Fig. 2) were determined on an open-scale plot: R, M, N, V, and the break in the 500° and the 600° isotherms.

The other field, M–N–K–F, of which M–N (Fig. 2) is a common boundary, contains two solid solutions—chalcocite and intermediate—both of which segregate during cooling. The resulting textures are largely determined by the texture of the grains before heating.[1] If the charge was prepared from a coarse grained matte then the segregated texture of the final grains is correspondingly extensive.

If approach is made from the high-sulphur side and new crystals form by reactions which break up the original crystals the new textures tend to be disordered and very fine-grained, also unstable phases are more likely to appear. For example, the fields containing chalcopyrite (intermediate solid solution) and Cu_2FeS_3 are not neighboring, but the fine-grained products from heating pyrite and Cu_2FeS_3 so as to produce chalcocite solid solution (within the field R–M–FeS_2, Fig. 2), often contained small amounts of a constituent resembling chalcopyrite (unstable).

From the high-sulphur side at 540°, the two preparations 23[h] and 25[h] contain abundant chalcocite solid solution, mostly without associated intermediate solid solution. A little of the latter, presumably unstable, is present. Thus, solid solution in chalcocite extends to or slightly beyond the angle in the 540° isotherm. Chalcopyrite which had been converted previously into pyrite and chalcocite solid solution, $(CuFeS_2)$,[h] when now heated at 560° contains at equilibrium, chalcopyrite solid solution from which chalcocite solid solution segregates on cooling. Thus, the intermediate (chalcopyrite) solid solution extends beyond the angle in the 560° isotherm.

From the low sulphur side the 4 : 1 was originally a very coarsely crystalline homogeneous chalcocite solid solution. By absorbing sulphur at 540° it has passed into the field M–F–K–N near M (Fig. 2), and contains about 20 per cent. of rudely faceted equant grains (probably slightly enlarged by unmixing) of intermediate solid solution, oriented in a matrix of chalcocite solid solution.[2] Assuming the former to have a composition near N, the latter must have a composition near 5 : 1 on the 540° isotherm, but the 5 : 1 on this isotherm contains a little unmixed intermediate solid solution—in lamellæ parallel to the cube (see Table 8). Thus, according to the phase relations the limit of the chalcocite solid solution on the 540° isotherm is between 4 : 1 and 5 : 1 on the line R–M–N, and is in accord with the limit at 550°. The point M is thus established.

The following data locate points close to the boundary M–F: the 4 : 1 at 750° contains relatively few yellow grains, and at 850° none; the 3 : 1 at 850°, and the 2.7 : 1 and 2.5 : 1 mattes contain scattered coarse irregular gash-like yellow bodies that appear to be mostly products of unmixing, but probably had original yellow nuclei. Then M–F is nearly straight, and the coordinates of F are: Fe = 18.0, S = 26.9.

By the same method N–K is found. The 2 : 1 at 750° consists of crystals of yellow intermediate solid solution with a few per cent. of interstitial chalcocite solid solution, which has disappeared between 667° and 605°—from which N is near Fe = 21.3, S = 30.5. Each of these phases has unmixed and contains fine gash-like bodies of the other.

At 1½ : 1, 900°, 50 mm., interstitial chalcocite solid solution is present, but at 850°, 455 mm., it is present only in traces. This point is Fe = 25.8, S = 30.4. The 1 : 1 mattes, Nos. 27 and 66, are within the area of the chalcopyrite-$Cu_5Fe_4S_6$ solid solution. By interpolation K is Fe = 29.0, S = 30.5.

[1] Within a grain at high temperature, scattered remnants or new growth of a solid solution phase with which the grain is saturated, may serve as nuclei for segregation during cooling, and thus prevent supersaturation and the attendant finer grained segregation texture.

[2] But for lag, 0.3 more sulphur should have been absorbed, and the chalcopyrite changed into pyrite and chalcocite solid solution.

TABLE 29. PARTIAL ISOTHERM 520°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 31).
14	5 : 1	63.24	10.81	25.95	3	Orange + a little yellow, no py.
16	4 : 1	59.97	12.92	27.11	3	Orange + several per cent. soft yellow grains + pyrite.
19	3 : 1	54.53	15.85	29.62	3	Orange + trace soft yellow + py.
22	2 : 1	46.80	20.12	33.08	3	Orange + soft yellow + pyrite.
23	1⅔ : 1	43.0	22.5	34.5	3	Orange + pyrite + some soft yellow. Many grains had no yellow.
24	1.5 : 1	41.25	23.32	35.43	3	Orange + pyrite + some soft yellow. Many grains had no yellow.
25	1⅓ : 1	37.84	25.39	36.77	3	Orange + pyrite, trace of soft yellow.
($CuFeS_2$)	1 : 1	32.39	28.39	39.22	3	Orange + pyrite, trace of soft yellow.

TABLE 30. ISOTHERM 500°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 31).
61 (465)	5 : 1	62.04	11.09	26.87	2	Orange + traces of soft yellow and py.[a]
		62.13	11.01	26.86		
14	5 : 1	63.01	10.79	26.20	3	Orange + a little soft yellow and py.
16	4 : 1	59.29	12.78	27.93	3	Orange + pyrite.
19	3 : 1	53.93	15.88	30.19	3	
22	2 : 1	46.54	20.11	33.35	3	
23	1⅔ : 1	42.60	22.35	35.05	3	
24	1½ : 1	40.31	23.63	36.06	3	
25	1⅓ : 1	37.91	24.97	37.12	3	
69 (465)	1 : 3	14.42	38.37	47.21	2	

[a] Two different charges at same heating.

TABLE 31. ISOTHERM 490°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Table 1).
58	6 : 1	64.88	9.60	25.52	2	Orange + mere trace soft yellow.
60	5 : 1	62.92	10.90	26.17	1	Orange + soft yellow, trace py.
63	4 : 1	59.09	12.87	28.04	2	Orange + a little pyrite.
64	3 : 1	53.78	15.83	30.39	2	Orange + py. + trace soft yellow.
64	3 : 1	53.54	15.80	30.66	1	Orange + pyrite.
65*A*	2 : 1	46.20	20.30	33.50	2	
		45.92	20.26	33.82	1	
($CuFeS_2$)	1 : 1	31.87	28.28	39.85	1	Orange + pyrite. These were not heated long enough.
(Cubanite)	1 : 2	—	—	—	1	
68	1 : 2	19.99	35.41	44.60	2	
69	1 : 3	14.91	39.51	45.58	2	Orange + py. with cores of pyrr.

Tables 29 to 31.—At these temperatures as well as others between 550° and 484° the equilibrium products for ratios of Cu to Fe less than 5 or 6 to 1 contain pyrite and chalcocite solid solution. The latter changes composition, as the temperature falls, from M to R. Most of these preparations during heating, as sulphur is being absorbed, develop grains of the soft yellow phase as an intermediate product. These disappear at these temperatures as pyrite forms. But after three heatings considerable amounts remain in the 4 : 1 product at 520°, whereas no grains should remain below about 550°. The soft yellow gashes form during cooling as the chalcocite solid solutions change toward pure chalcocite. Many grains, however, do not thus unmix.

TABLE 32. DATA AT 482°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 35).
2	—	—	—	—		Originally gray Cu_2S. Now blue CuS.
3	—	70.63	0.93	28.44	2	Covellite + gray.
3	—	69.62	0.98	29.40	2	60 per cent. covellite + 40 per cent. gray (approximately).
5	16.3 : 1	72.70	3.90	23.40	2	Dark gray.
5	16.3 : 1	72.51	3.87	23.62	2	Dark gray.
53	14 : 1	71.81	4.52	23.67	2	Dark gray.
53	14 : 1	71.71	4.51	23.78	2	Dark gray.
54	9 : 1	68.60	6.75	24.65	2	Brownish gray + trace of bronze.
54	9 : 1	68.61	6.73	24.66	2	Brownish gray + trace of bronze.
56	7 : 1	66.57	8.19	25.24	2	Orange-gray + trace of bronze.
56	7 : 1	66.30	8.11	25.59	2	Orange-gray + bronze.
12	6 : 1	62.73	9.16	28.11	2	Orange-gray + bronze.
12	6 : 1	63.62	9.33	27.05	2	Orange-gray + a little bronze + trace py.
12	6 : 1	58.87	8.65	32.48[a]	2	Bronze + orange-gray + trace pyrite.
14	5 : 1	61.03	10.39	28.58	2	Orange-gray + bronze.
61	5 : 1	60.35	10.58	29.07	2	Orange-gray + bronze.
61	5 : 1	55.91	9.92	34.17[a]	2	Bronze + trace pyrite.
16	4 : 1	58.29	12.61	29.10	2	Orange-gray + bronze + trace py.
16	4 : 1	58.37	12.73	28.90	2	Orange-gray + bronze + pyrite.

TABLE 32 (*Continued on next page*)

TABLE 32 (*Continued*).

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Tables 1 and 35).
16	4 : 1	53.26	11.64	35.10[a]	2	Bronze + pyrite.
23		39.26	20.87	39.87[a]	2	
23[b]	1⅞ : 1	39.38	20.70	39.92[a]	2	
23		39.77	20.90	39.33[a]	2	Bronze + pyrite.
25[b]	1⅛ : 1	35.51	23.55	40.94[a]	2	
($CuFeS_2$)[b]	1 : 1	30.51	26.74	42.75[a]	2	

[a] At same heating.

TABLE 33. DATA AT 480°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases (see Tables 1 and 35).
3	—	68.98	0.96	30.06	2	*ca.* ¾ covellite + gray.
4	29 : 1	66.19	2.12	31.69	2	*ca.* ½ covellite + gray.
5	16 : 1	71.93	3.89	24.18	2	Gray + covellite.
53	14 : 1	71.52	4.52	23.96	2	Gray.
6	11 : 1	70.14	5.67	24.19	2	Gray.
7	10 : 1	68.09	6.31	25.60	2	Gray + bronze.
54	9 : 1	68.55	6.74	24.71	2	Orange-gray + a little bronze.
56	7 : 1	65.65	8.15	26.20	2	Orange-gray + bronze.
12	6 : 1	60.23	8.95	30.82	2	Bronze + orange-gray (?).
60	5 : 1	58.90	10.20	30.90	1	Bronze + orange-gray + pyrite.
61	5 : 1	57.08	10.13	32.79	1	Bronze + pyrite.
16	4 : 1	55.94	12.16	31.90	2	Bronze + pyrite.
19	3 : 1	49.19	14.40	36.41	2	Bronze + pyrite.
65*A*	2 : 1	45.3	19.4	35.3	2	Bronze + pyrite.
$CuFeS_2$	1 : 1	30.20	26.88	42.92	1	Bronze + pyrite.
$CuFeS_2$	1 : 1	31.92	28.26	39.82	1	Orange-gray + pyrite (+ a little bronze and covellite).
36	1 : 2	20.46	36.00	43.54	1	Orange-gray + pyrite (+ residual soft yellow).

TABLE 33*A*. PARTIAL ISOTHERM 479°, 455 MM.
ALL AT ONE 6-HOUR HEATING.

Cu : Fe Molal.	Composition Wt. %. Cu.	Fe.	S.	Original S.	
29 : 1	69.87	2.14	27.99	33.55[a]	Covellite + gray.
	69.92	2.10	27.98	21.57[b]	
14 : 1	70.02	4.32	25.66	33.76[a]	Gray + covellite + trace bronze.
	71.50	4.48	24.02	23.73[b]	Gray + covellite.
7 : 1	62.24	7.64	30.12	33.90[a]	Gray + bronze-colored.
	62.97	7.73	29.30	23.90[b]	

[a] Containing covellite and $Cu_{5+}FeS_{6+}$.
[b] Mattes.

TABLE 34. ISOTHERM 476–8°, 455 MM.
12-HOUR HEATINGS.

Matte Used.	Cu : Fe Molal.	Composition Wt. %. Cu.	Fe.	S.	Phases.
3	—	67.36	0.89	31.75	
3	—	67.45	.91	31.64	
3	—	68.03	.94	31.03	
4	29 : 1	68.95	2.12	28.93	Gray + covellite.
4	29 : 1	70.60	2.20	27.20	
5	16 : 1	70.15	3.77	26.08	
5	16 : 1	70.84	3.75	25.41	
53	14 : 1	71.63	4.51	23.86	Gray, only.
8	9 : 1	65.27	6.65	28.08	Gray and bronze color, subequal.
56	7 : 1	61.53	7.59	30.88	Bronze-color and orange-gray.
56	7 : 1	61.70	7.68	30.62	Bronze-color and orange-gray.
12	6 : 1	58.39	8.55	33.06	Bronze-color and some orange-gray.
12	6 : 1	58.51	8.58	32.91	Bronze-color and some orange-gray.
12	6 : 1	59.18	8.70	32.12	Bronze-color and some orange-gray.
13	5.4 : 1	56.87	9.48	33.65	Bronze-color.
61	5 : 1	55.89	9.83	34.28	Bronze-color and some pyrite.
61	5 : 1	55.95	9.90	34.15	Bronze-color and some pyrite.
61	5 : 1	55.90	9.93	34.17	Bronze-color and some pyrite.
16	4 : 1	53.56	11.47	34.97	
16	4 : 1	53.38	11.68	34.94	Bronze-color and pyrite.
19	3 : 1	49.87	14.37	35.76	
19	3 : 1	49.19	14.40	36.41	

TABLE 34*A*. PARTIAL ISOTHERM 475°, 455 MM.
ALL AT ONE 6-HOUR HEATING.

Cu : Fe Molal.	Composition Wt. %. Cu.	Fe.	S.	Original S.	Phases.
29 : 1	67.39	2.11	30.50	33.55[a]	Covellite + gray.
	68.69	2.15	29.16	21.57[b]	
14 : 1	68.05	4.23	27.72	33.76[a]	Gray + cov. (+ residual bronze).
	71.47	4.54	23.99	23.73[b]	Gray + a little covellite.
7 : 1	60.98	7.42	31.60	33.90[a]	Bronze + gray.
	62.00	7.62	30.38	23.90[b]	

[a] Contain covellite and $Cu_{5+}FeS_{6+}$.
[b] Mattes.

TABLE 34*B*. PARTIAL ISOTHERM 470°, 455 MM. 6-HOUR HEATINGS.

Matte Used.	Cu : Fe Molal.	Composition Wt. %. Cu.	Fe.	S.	Phases.
56	7 : 1	58.70	7.25	34.05	Bronze + covellite.
12	6 : 1	57.83	8.33	33.84	Bronze + covellite.
12	6 : 1	57.72	8.54	33.74	Bronze + covellite.
59	5 : 1	56.06	9.91	34.02	Bronze.
63	4 : 1	53.35	11.55	35.09	Bronze + pyrite.
$CuFeS_2$	1 : 1	30.34	26.82	42.84	Bronze + pyrite.
$CuS + FeS_2$	1 : 1	—	—	—	Slight reaction to form bronze-color.

TABLE 35. DATA FOR 465°–460°, 455 MM.

Matte Used.	Cu : Fe (Molal).	Temp. °C.	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Description of Phases, and Remarks (see Table 1).
3	—	460	65.37	1.14	33.49	2	Bronze-colored + cov.
4	29 : 1	465	64.40	2.05	33.55	2	
53	14 : 1	465	62.36	3.88	33.76	2	
12	6 : 1	465	57.61	8.44	33.95	3	Bronze-colored, little cov.
13	5.3 : 1	465	56.49	9.36	34.15	2	Bronze-colored + pyrite.
13	5.3 : 1	465	56.74	9.39	33.87	3	
61	5 : 1	465	55.87	9.83	34.30	3	
22	2 : 1	465	42.90	18.33	38.77	3	
23	1⅔ : 1	460	39.26	20.75	39.99	3	
25	1½ : 1	460	34.92	23.67	41.41	3	
27	1 : 1	465	30.45	26.61	42.93	3	
$CuFeS_2$	1 : 1	460	30.12	26.71	43.17	3	
$CuS + FeS_2$	1 : 1	460	—	—	—	1	A little bronze-colored formed.
32	1 : 1⅓	460	25.73	29.85	44.42	3	Bronze-colored + pyrite.
36	1 : 2	460	19.53	34.11	46.36	3	

Tables 32–35.—The data of these tables show that marked increases in sulphur content and conspicuous changes in phase relations take place within an interval of decreasing temperature of 20°. These changes result from the reactions of three different chalcocite solutions with sulphur: (1) iron-free chalcocite changes to covellite at 488°; (2) the iron- and sulphur-rich chalcocite, R, reacts with sulphur and pyrite to form Cu_5FeS_6 at 484°; and (3) an intermediate chalcocite solid solution, P, and sulphur forms a mixture of covellite and $Cu_{5+x}FeS_{6+x}$ at 472°.

Thus, covellite is stable with a series of chalcocite solid solutions from ∞ : 1 to about 12 : 1 successively as the temperature decreases from 488° to 472° (Tables 32–34) and isotherms radiate from covellite to these chalcocite solid solutions. Each of these isotherms passes into the chalcocite field and continues there subparallel with those at higher temperatures. One of these isotherms, 484°, expands into an isothermal field R-Cu_5FeS_6-FeS_2. The compositions 5 : 1 to 2 : 1 of Tables 32 and 33 are within this field although with prolonged heatings enough sulphur would have been absorbed to carry the compositions through the field. Within the field the stable phases are the chalcocite solid solution R (Fig. 2), pyrite, and Cu_5FeS_6. The identification of small amounts of the first in presence of much of the last is almost impossible because those sections of the last which are nearly isotropic are similar to the first in color.

The heatings of Tables 33*A* and 34*A*, in which sulphur was evolved, started with mixtures of covellite and $Cu_{5+x}FeS_{6+x}$ made by preheating mattes at 460° and 455 mm. The final products and compositions agree well with those arrived at by absorption of sulphur at similar temperatures. Specifically, at 465°, and even at 470°, absorption

of sulphur has gone essentially to completion with respect to these three reactions, but at the [illegible] heating chalcocite solid solution is one of the phases, therefore an intermediate temperature, 472°, is the inferred temperature of the reaction sulphur + P $\rightleftarrows$ covellite + $Cu_{5+}FeS_{6+}$, with P—according to the phase change—on the chalcocite solid solution boundary between 14 : 1 and 7 : 1; the narrower limit, 14 : 1 to 11 : 1, is indicated in Table 33, and plotting all the results leads to coördinates given in the legend of Fig. 2.

Tables 34 and 35, also 40 and 41, 6 : 1 and 5.3 : 1 show that solid solution of covellite in Cu_5FeS_6 extends almost to 6 : 1. A straight line from this point, T, to P is one of the isothermal boundaries of the field produced by the reaction just mentioned. This isotherm extends to FeS_2.

Slowness in approaching equilibrium, and experimental errors of perhaps 3°, account for the obvious differences in compositions. (See discussion of Tables 37–41.)

TABLE 36. DATA AT 450°–411°, 455 MM.

Material Used.	Cu : Fe (Molal).	Temp. °C.	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Phases (see Tables 1 and 41A).
$CuS + FeS_2$	1 : 1	450	—	—	—	1	No definite reaction products seen.*
Chalcopyrite	1 : 1	450	30.12	26.85	43.03	1	All changed to py. + bronze-colored.
Chalcopyrite	1 : 1	430	30.08	26.75	43.17	1	All changed to py. + cov. (+ bronze-colored).
Chalcopyrite	1 : 1	420	29.75	26.57	43.68	1	All changed to py. (+ bronze-colored) + cov.
Matte	5 : 1	420	—	—	—	1	
Bronze	5 : 1	420	—	—	—	1	Bronze-colored + pyrite + trace cov.
Bronze	5 : 1	411	—	—	—	1	Bronze-colored + pyrite + trace cov.
Matte	5 : 1	411	—	—	—	1	All changed to pyrite + bronze + cov.
Matte	5 : 1	411	—	—	—		Heated 15 minutes. Thick coating of covellite over cores of unchanged matte + bronze + soft yellow.

* At 440°—300 mm. (closely comparable with 450°—455 mm.) definite reaction.

Table 36.—At temperatures definitely below 460°, and probably just below 450°, mixtures of covellite (CuS) and pyrite (FeS_2) react slowly by eliminating sulphur to form the bronze-colored crystals $Cu_{5+}FeS_{6+}$. At 450° compositions already low in sulphur absorb only enough sulphur to form the bronze-colored compound. Only at a temperature between 450° and 430°, has this compound then reacted further to give covellite. Also, once formed, further reaction is slow unless equilibrium is much overstepped—practically no covellite at 420° or 411° (Table 36), or in saturated sulphur vapor, 445°—760 mm. (Table 41A). But if a low-sulphur matte in which the bronze-colored compound is not originally present is thus heated covellite (with pyrite or chalcopyrite) forms immediately, and in a few minutes, abundantly as a surface concentrate. The interiors thus protected and enriched in iron react slowly and show intermediate products. Small lumps of a 5 : 1 matte heated 6 hours at 411° showed a roughly concentric arrangement: pure covellite; bronze-colored dotted with pyrite; bronze-colored with streaks of chalcopyrite solid solution grading into a core of chalcocite solid solution. Large grains of 1 : 1 matte after 6 hours heating showed a surface layer of covellite with pyrite grains near the base, then a zone of chalcocite solid solution peppered with pyrite, and a core of chalcopyrite.

TABLE 36*A*. COÖRDINATES OF ISOTHERMS,[a] 455 MM.

	480°.					500°.		
	Covellite.	G–P.	P–R.	Cu_5FeS_6 –T.	Pyrite.	Chalcocite s.s.	R–M.	Pyrite.
Cu	66.5	74.0	68.1	56.5	—	77.5	65.3	—
Fe	—	2.7	7.2	9.5	46.5	—	9.4	46.5
S	33.5	23.3	24.7	34.0	53.5	22.5	25.3	53.5

	550°.					600°.					
	Chalcocite s.s.[b]	5 : 1.[b]	M.[b]	N.[b]	Pyrite.	Chalcocite s.s.[b]	5 : 1.[b]	M–F.[b]	N–K.[b]	N–V.	Pyrite.
Cu	77.54	63.00	59.6	48.2	—	77.64	63.00	59.4	48.0	36.2	—
Fe	—	11.05	13.4	21.3	46.5		11.07	13.6	21.5	29.8	46.5
S	22.46	25.95	27.0	30.5	53.5	22.36	25.84	27.0	30.5	34.0	53.5

	650°.						
	Chalcocite s.s.[b]	5 : 1.[b]	M–F.[b]	N–K.[b]	1 : 1.	V–L.[b]	Pyrite.
Cu	78.78	63.15	58.9	47.3	35.2	29.4	
Fe	—	11.10	14.1	22.2	31.0	35.4	46.5
S	22.22	25.75	27.0	30.5	33.8	35.2	53.5

[a] Others in Table 17*A*.
[b] The last figure is significant but not accurate.

TABLE 37. ISOTHERM 540°, 760 MM.

Matte ed.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Phases (see Tables 1 and 41).
1	—	77.51	—	22.49	3	Bluish gray.
60_{470}	5 : 1	62.80	10.84	26.36	1	Orange with yellow gashes + bronze (residual).
60	5 : 1	63.10	10.93	25.97	3	Orange with yellow gashes.
63	4 : 1	59.67	12.89	27.44	3	Orange + a little soft yellow + py.
64	3 : 1	54.12	15.95	29.93	3	
64_{470}	3 : 1	53.84	15.92	30.24	1	
65*A*	2 : 1	46.40	20.33	33.27	3	Orange + pyrite.
65_{470}	2 : 1	46.13	20.34	33.53	1	
$CuFeS_2$	1 : 1	32.26	28.47	39.27	3	
68	1 : 2	20.01	35.37	44.62	3	

TABLE 38. HEATINGS AT 500°, 760 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Phases (see Tables 1 and 41).
1	—	77.69	—	22.31	1	Homogeneous, bluish gray.
4	29 : 1	74.50	2.29	23.21	1	Homogeneous, bluish gray.
52	17 : 1	72.75	3.62	23.63	1	Homogeneous, dark gray.
53	14 : 1	71.77	4.50	23.73	1	Homogeneous, dark gray.
6	11 : 1	70.24	5.64	24.12	1	Homogeneous, gray.
54	9 : 1	68.49	6.75	24.76	1	Orange-gray.
55	7 : 1	66.33	8.46	25.21	1	
58	6 : 1	65.06	9.51	25.43	1	
60	5 : 1	63.13	10.86	26.01	1	Orange-gray + *ca.* 10 per cent. soft yellow.

TABLE 39. HEATINGS AT 490°, 760 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Phases (see Tables 1 and 41).
1	—	66.53	—	33.47	1	Originally Cu_2S, now CuS (cov.).
4	29 : 1	73.45	2.31	24.24	1	Bluish gray + a little cov.
52	17 : 1	72.72	3.62	23.66	1	+ Trace covellite and bronze.
53	14 : 1	71.47	4.67	23.86	1	Uniformly, nearly neutral gray.
6	11 : 1	70.08	5.57	24.35	1	
54	9 : 1	68.59	6.76	24.65	1	Orange-gray + trace cov. and bronze.
55	7 : 1	65.33	8.31	26.36	1	Orange-gray + bronze + trace surficial cov.
58	6 : 1	63.46	9.30	27.24	1	Bronze + orange-gray + trace soft yellow.
60	5 : 1	60.55	10.38	29.07	1	Orange-gray + bronze + py. + trace soft yellow.
	5 : 1	61.90	10.74	27.36	1	Orange-gray + py. + a little soft yellow + bronze.
	1 : 3	14.56	38.79	46.65	2	Orange-gray + pyrite, incomplete reaction.
	1 : 5	9.79	41.88	48.33	2	

TABLE 40. HEATINGS AT 480°, 760 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Phases (see Tables 1 and 41).
1	—	66.38	—	33.62	1	Originally Cu_2S, now CuS (cov.).
4	29 : 1	69.81	2.17	28.02	1	Bluish gray + covellite.
52	17.4 : 1	72.10	3.60	24.30	1	
53	14 : 1	71.05	4.49	24.46	1	Dark gray + a little covellite.
53	14 : 1	71.64	4.61	23.75	1	Dark gray.
6	11 : 1	69.82	5.58	24.60	1	Dark neutral gray (bronze + cov., on cooling).
6	11 : 1	70.22	5.59	24.19	1	Dark gray.
54	9 : 1	67.06	6.61	26.33	1	Orange-gray + *ca.* 20 per cent. bronze.
54	9 : 1	68.45	6.75	24.80	1	Orange-gray + a little bronze.
55	7 : 1	61.32	7.84	30.84	1	Orange-gray + bronze—subequal.
55	7 : 1	60.58	7.73	31.69	1	Bronze + *ca.* 20 per cent. gray.
56	7 : 1	62.57	7.75	29.68	1	Bronze + gray.
55	7 : 1	61.99	7.86	30.15	1	
55	7 : 1	61.73	7.92	30.35	1	
58	6 : 1	58.55	8.54	32.91	1	
57	6 : 1	58.35	8.48	33.17	1	
60	5 : 1	56.24	9.69	34.07	1	Bronze + pyrite.
63	4 : 1	53.40	11.50	35.10	1	
45	1 : 19	3.01	49.41	47.58	1	Pyrite coating on pyrrhotite.
46	1 : 33	1.70	49.55	48.75	1	

TABLE 41. HEATINGS AT 470°, 760 MM.

Matte Used.	Cu : Fe (Molal).	Composition Wt. %. Cu.	Fe.	S.	Heatings.	Phases (see Table 1).
4	29 : 1	64.50	1.99	33.51	1	Covellite + bronze.
52	17 : 1	63.18	3.15	33.67	1	
53	14 : 1	62.47	3.96	33.57	1	
6	11 : 1	61.24	4.89	33.87	1	
54	9 : 1	60.25	5.92	33.83	1	Bronze + covellite.
55	7 : 1	58.65	7.44	33.91	1	Bronze + covellite.
58	6 : 1	57.72	8.47	33.81	1	Bronze + *ca.* 2½ per cent. cov.
60	5 : 1	56.17	9.67	34.16	1	Bronze + traces pyrite.
	4 : 1 to 1 : 5				2	Bronze + pyrite.

Tables 37–41 (*q.v.*).—Comparison by plotting of practically identical compositions at 540°—760 mm. with 520°—455 mm. shows that equilibrium was reached at the longer heatings at 540°, but not quite at 520° for 4 : 1 and 3 : 1 in which the lag in the formation of pyrite is notable. Long heatings, however, were not necessary at ratios of Cu to Fe higher than 5 : 1. Even at the slower reaction velocities at 455 mm., 6-hour heatings gave the essential data. (Tables 33*A* and 34*A*.)

The reactions at 760 mm. are as follows:

$CuS \rightleftarrows Cu_2S_{1+}$ + sulphur (497°). See Tables 38, 39 and 10*A*.

Chalcocite s.s. (P′) + sulphur $\rightleftarrows$ CuS + $Cu_{5+}FeS_{4+}$ (477°). See Tables 40–41.

Chalcocite s.s. (R′) + sulphur + pyrite $\rightleftarrows$ Cu_5FeS_6 (490°–500°). See Tables 38–39.

$Cu_{5+}FeS_{6+}$ + sulphur $\rightleftarrows$ CuS + FeS_2 (> 445°, < 470°). See Tables 41, 41*A*.

In the heatings at temperatures 470° to 500° the temperature of the sulphur was not far below that of the sulphide, therefore when using the usual procedure of removing

the sulphur bulb from the furnace after the sulphide bulb had begun to cool, there was created for a few seconds, at the more rapidly cooling exposed surface of each little charge of sulphide, an excess sulphur pressure. This was sufficient to cause the surfaces of grains of the most sulphur-rich chalcocite solid solutions from α : 1 to 7 : 1, to react somewhat with sulphur to produce covellite and $Cu_{5+}FeS_{6+}$. This surface was rejected before analysis. Similarly, surface grains containing much $Cu_{5+}FeS_{6+}$ became coated with covellite, while within there developed a sprinkling of soft yellow particles which, according to Fig. 2, must be chalcopyrite (unstable).

From the low-sulphur side, while the charges of Tables 30 to 41 were being brought up to temperature the two bulbs were heated at about the same rate, therefore the formation of a coat of covellite on grains must have taken place (see also Table 41*A*). The incomplete recombination to homogeneous grains of this covellite with the iron-enriched cores may account in part for the slightly high sulphur values of some of the preparations at 14 : 1 to 9 : 1 near 480°, 760 mm. and 455 mm.

TABLE 41*A*. HEATINGS IN SATURATED SULPHUR VAPOR.[1]

Substance Heated.	Cu : Fe (Molal).	Temp. °C.	Time Min.	Phases (see Table 1).
—A. Short Heatings.—				
Matte	5 : 1	390	*ca.* 1	Coating of covellite over yellow-streaked orange-colored.
			ca. 3	As above with thicker covellite.
		411	15	Thick covellite over bronze-colored with cores of yellow-streaked orange-colored.
Chalcopyrite	1 : 1	390	*ca.* 3	Slight tarnish.
			21	Distinct film of covellite over soft yellow.
—B. Heating for 4 to 6 hours.[1]—				
Bornite	5 : 1	470	(1086 mm.)	Changed to bronze-colored and pyrite.[a]
Bronze-colored Cu_5FeS_6	5 : 1	445	(760 mm.)	Remained bronze-colored with development of a little pyrite. Mere traces of covellite.
		411	(455 mm.)	
		390	(320 mm.)	
		350	(152 mm.)	
Matte	5 : 1	445	(760 mm.)	Thick covellite, over pyrite in bronze-colored and soft yellow
		411	(455 mm.)	Much covellite with pyrite over bronze-colored.
		390	(320 mm.)	
		350	(152 mm.)	
Matte	1 : 1	390	(320 mm.)	Completely changed to covellite and pyrite.
		350	(152 mm.)	Mostly changed to covellite and pyrite.
Matte	1 : 2	390	(320 mm.)	Soft yellow surrounded by grains of pyrite in covellite.
		350	(152 mm.)	

[1] See discussion Table 36.

[a] Analysis: Cu = 55.66, Fe = 9.98, S = 34.36.

Table 41A.—At 350° and 390° the minute hard grains when polished had rounded surfaces upon which no distinct anisotropy was observed. Marcasite here probably would show anisotropy.

According to Allen and Crenshaw (Am. J. Sci., vol. 38, 393, 1914) marcasite slowly changes to pyrite as low as 350°, but it forms in solutions as high as 300°. For studies by means of x-rays see M. J. Buerger (Am. J. Sci., vol. 16, 361, 1931); F. M. Bannister (Min. Mag., vol. 23, 179, 1932); H. V. Anderson and K. G. Chesley (Am. J. Sci., vol. 25, 315, 1933). Anomalous results from a single specimen led the latter to conclude that powdering marcasite causes it to change to pyrite.

TABLE 42. A. CHALCOPYRITE HEATED AT 300 MM.

Temp., ° C.	S, Wt. %.	Heatings.	Phases.
490	39.7	1	Pyrite + chalcocite solid solution.
470	39.9	1	Pyrite + chalcocite solid solution + a little Cu_5FeS_6.
470	43.0	1	Pyrite + Cu_5FeS_6.
450	43.0	1	Same.
430	40.1	1	Pyrite + chalcocite s.s.
	42.8	1	Pyrite + Cu_5FeS_6, no covellite.
	42.9	2	Same.
	43.0	3	Same.
410	43.3	1	Pyrite + covellite, with much unchanged $Cu_{5+}FeS_{6+}$.
	43.7	2	
	43.9	3	

B. MIXTURES OF COVELLITE AND PYRITE HEATED AT 300 MM.

440	—	1	No change observed.
	—	2	Traces of $Cu_{5+}FeS_{6+}$.
450	—	1	Much $Cu_{5+}FeS_{6+}$.

TABLE 43. 6-HOUR HEATINGS OF 1 : 1 MIXTURES OF COVELLITE AND PYRITE AT 58 MM.

Temp., ° C.	S, Wt. %.	Phases.
420		No reaction observed.
430		Slight reaction to form $Cu_{5+}FeS_{6+}$ (residual covellite and pyrite).
440		Decided reaction.
450		$Cu_{5+}FeS_{6+}$ + gray chalcocite [a] solid solution (residual covellite and pyrite).
460		$Cu_{5+}FeS_{6+}$ + chalcocite solid solution (residual covelite [b] and pyrite).
470		Same, but no covellite.
500		Only traces of Cu_5FeS_6 [c]; chalcocite s.s. + (py.).
520	39.9	Chalcocite solid solution (pyrite).
540	39.6	Chalcocite s.s. (and py.) but no cp. (chalcopyrite).
550	39.3	Chalcocite s.s. (and pyrite) + some cp.
560	39.4	Chalcopyrite solid solution (residual py. and chalcocite s.s.).
570	38.6	Same.
580	37.6	Largely chalcopyrite s.s. from which chalcocite s.s. has segregated.
600	36.1	Chalcopyrite s.s. + a few per cent. pyrite.
630	34.4	Homogeneous chalcopyrite s.s.

[a] This contains iron. Pure chalcocite would not form here from covellite.
[b] Long heating at 458° (Table 10A) changes covellite to pure chalcocite.
[c] Cu_5FeS_6 disappears slowly here, even with the equilibrium overstepped about 40°.

Temp., ° C.
580
570
550
525
500
470
450
450
420
400
400

TABLE 44. 6-HOUR HEATINGS OF CHALCOPYRITE AT 58 MM.

Temp., °C.	S, Wt. %.	Phases.
580	34.2	Homogeneous.
570	35.5	Chalcopyrite s.s.; traces of segregated chalcocite s.s.; pyrite.
550	36.1	As above but with more py. and chalcocite s.s.
525	37.8	Chalcopyrite s.s. with intricate fine pattern of segregated chalcocite s.s. formed during cooling; pyrite.
	38.4	Chalcocite s.s. with elongated bodies of chalcopyrite s.s., probably partly residual and partly unmixed; pyrite.
	38.8	As above, but only a little chalcopyrite s.s.
500	39.3	Chalcocite s.s. with a little (probably unmixed) chalcopyrite s.s.; pyrite.
470	39.8	Chalcocite s.s. + pyrite.
450	39.8	do.
450	42.8	Cu_5FeS_6 + pyrite.
420	42.9	do.
400	43.2	Covellite and pyrite (and much residual Cu_5FeS_6).
400	44.0	Covellite and pyrite (and little Cu_5FeS_6). Sample heated 12 hours.

TABLE 45. SOME DATA ON MELTING.[a]

Cu : Fe (Molal).	Temp. ° C.	Pressure.	Composition Wt. %. Cu.	Fe.	S.	Remarks.	Ref.
∝ : 1	1130	vac.	79.8	—	20.2	At melting temp.	1
	1096	(H_2S) [b]	78.7		21.(3)	At melting temp.	1
	1057	(760 mm.) [b]	77.7		22.3	At melting temp.	1
5 : 1	1085 ± 15	455 mm.	79.1	—	20.9	Estimated beginning of melting	—
	950–1025	>1 atm.		—		Various bornites melted	7
	1000	58 mm.				Not melted	7
4 : 1	1000	58 mm.				Not melted	7
	950	455 mm.				Not melted	7
3 : 1	1080	H_2S	57.0	16.7	26.3	Melted	Table 5
	950	58 mm.				Not melted	7
1½ : 1	920	H_2S				Not melted	7
1 : 1	1000	*ca.* 13 atm.	35.6	31.6	32.8	Above melting	7
	1000	*ca.* 8 atm.	35.8	31.7	32.5	Above melting	7
	875 ± 10	*ca.* 2 atm.	35.0	31.0	34.0	Estimated beginning of melting	—
	900	455 mm.	36.1	31.8	32.1	Not melted	Table 16
	935	H_2S	36.5	32.1	31.4	Incipient melting (?)	7
	925	2 mm.	36.7	32.4	30.9	Incipient melting (?)	Table 9
1 : 1.2	925	2 mm.				Not melted	Table 9
1 : 1.3	920	H_2S	31.1	36.0	32.9	Not melted	7

TABLE 45 (*Continued on next page*)

TABLE 45 (*Continued*).

Cu : Fe	Temp.		Composition Wt. %.				
(Molal).	° C.	Pressure.	Cu.	Fe.	S.	Remarks.	Ref.
1 : 1.4	920	H_2S	30.2	37.0	32.8	Not melted	7
1 : 1.5	920	H_2S	29.3	38.0	32.7	Not melted	7
1 : 1.6	920	H_2S	28.4	39.0	32.6	Not melted	7
1 : 1.7	920	H_2S	27.5	40.0	32.5	Not melted	7
1 : 1.8	920	H_2S	26.6	41.0	32.4	Not melted	7
1 : 1.9	920	H_2S	25.7	42.0	32.3	Not melted	7
1 : 2	920	H_2S	24.8	43.0	32.2	Not melted	7
1 : 2.1	920	H_2S	23.9	44.0	32.1	Not melted	7
1 : 2.2	920	H_2S	23.0	45.0	32.0	Not melted	7
1 : 2.3	920	H_2S	22.1	46.0	31.9	Not melted	7
1 : 2.4	920	H_2S	21.2	47.0	31.8	Not melted	7
1 : 2.5	920	H_2S	20.3	48.0	31.7	Not melted	7
1 : 2.6	920	H_2S	19.4	49.0	31.6	Not melted	7
1 : 2.7	920	H_2S	18.5	50.0	31.5	Not melted	7
1 : 2.8	920	H_2S	17.6	51.0	31.4	Not melted	7
1 : 2.9	920	H_2S	16.7	52.0	31.3	Not melted	7
1 : 3	920	H_2S	15.8	53.0	31.2	Not melted	7
1 : 3.1	920	H_2S	14.9	54.0	31.1	Not melted	7
1 : 3.2	920	H_2S	14.0	55.0	31.0	Not melted	7
1 : 3.3	920	H_2S	13.1	56.0	30.9	Not melted	7
1 : 3.4	920	H_2S	12.2	57.0	30.8	Not melted	7
1 : 3.5	920	H_2S	11.3	58.0	30.7	Not melted	7
1 : 3.6	920	H_2S	10.4	59.0	30.6	Not melted	7
1 : 3.7	920	H_2S	9.5	60.0	30.5	Not melted	7
1 : 3.8	920	H_2S	8.6	61.0	30.4	Not melted	7
1 : 3.9	920	H_2S	7.7	62.0	30.3	Not melted	7
1 : 4	920	H_2S	6.8	63.0	30.2	Not melted	7
1 : 4.1	920	H_2S	5.9	64.0	30.1	Not melted	7
1 : 4.2	920	H_2S	5.0	65.0	30.0	Not melted	7
1 : 4.3	920	H_2S	4.1	66.0	29.9	Not melted	7
1 : 4.4	920	H_2S	3.2	67.0	29.8	Not melted	7
1 : 4.5	920	H_2S	2.3	68.0	29.7	Not melted	7
1 : 4.6	920	H_2S	1.4	69.0	29.6	Not melted	7
1 : 4.7	920	H_2S	0.5	70.0	29.5	Not melted	7
1 : ∝	920	H_2S				Not melted	7

TABLE 45 (*Continued*).

Cu : Fe (Molal).	Temp. ° C.	Pressure.	Composition Wt. %. Cu.	Fe.	S.	Remarks.	Ref.
	910	?		cubanite		Beginning of melting	2, 7
	910	760 mm.	23.5	41.5	35.0	Incipient melting (?)	7
1 : 2	920 ± 15	455 mm.	23.6	41.6	34.8	Estimated beginning of melting	—
	950	58 mm.				Melted	7
	900	58 mm.				Not melted	Table 10
	925	2 mm.	24.2	42.2	33.6	Not melted	Table 9
ca. 1 : 1 to 1 : 10	900 995		Eutectic (?) melting of various mixtures of Cu_2S and FeS				3 4
	1170 ± 5	vac.	—	63.5	36.5	Melting	5
	1183	H_2S				Main heat effect	5
	1165	H_2S				Not melted	5
0 : 1	1185	455 mm.		61.4	38.6	Estimated beginning of melting	—
	1187	760 mm.				Main heat effect	5
	985		Eutectic between troilite and iron				6

1. E. Posnjak, E. T. Allen, and H. E. Merwin, The Sulphides of Copper, ECON. GEOL., vol. 10, 491, 1915.
2. E. T. Allen, in paper by B. L. Johnson, ECON. GEOL., vol. 12, 521, 1917.
3. Fedotieff (Text Ref. 11).
4. Carpenter and Hayward (Text Ref. 11).
5. E. T. Allen, J. L. Crenshaw, J. Johnston, and E. S. Larsen, The Mineral Sulphides of Iron, Am. J. Sci., vol. 33, 255, 1912.
6. K. Miyazaki, Sci. Repts. Tohoku Imp. Univ., vol. 17, 877, 1928, and earlier investigators.
7. From notes not included in the tables. See section on melting.

[a] See p. 237.

[b] See discussion of Table.

Table 45.—The equilibrium studies have shown that for 455 mm. at 500° chalcocite contains about 1 per cent. more sulphur than at 900° (Table 14). A similar difference is inferred for 760 mm., by extrapolation from the chalcocite solid solution, Cu_3FeS_4, of Table 13. Thus, the chalcocite of Table 42 that melted at 1057° and contained 22.3 per cent. sulphur (as compared with 22.5 per cent. at 500° of Table 14) probably retained in supersaturated solid solution some of the excess sulphur that it absorbed while being heated to melting in the vapor of boiling sulphur. Also, with respect to H_2S, the analyses may not quite represent equilibrium.

Powdered mattes of 1½ : 1, 1 : 1, 1 : 1½, and 1 : 2 were similarly heated in H_2S at about 920°. Only the 1 : 2 melted.

TABLE 46. UNMIXING—HEATINGS IN SMALL SEALED EVACUATED TUBES.

Material.	Cu : Fe (Molal).	Temp. °C.	Time Days.	Remarks[a] (see Table 1).
A. Chalcocite solid solutions				
Between bornite and $Cu_2S_{1.11}$	29 : 1, 10 : 1, 6 : 1	400	1	All apparently homogeneous.
do	29 : 1	150	1	Apparently homogeneous.
do	10 : 1	150	1	Reticulate orange in gray.
do	6 : 1	150	1	Reticulate gray in orange.
Between bornite and Cu_2S	11 : 1	300	5	Unchanged.
		200	5	
		100	8	
0.6 per cent. S below line Cu_2S-bornite	6 : 1	300	5	Lamellæ of gray in very finely mottled orange.
		200	5	A few grains show the gray lamellæ.
		100	8	Gray lamellæ bordered by soft yellow in orange.
On the 490°—455 mm. isotherm	11 : 1	300	5	No change.
		200	5	
		100	8	Coarse lamellæ of orange in gray.
		87	11	Fine lamellæ of orange in gray.
∴ containing a little more sulphur than mixtures of bornite and $Cu_2S_{1.18}$	7 : 1	300	5	About 1 per cent. soft yellow in gray.
		200	5	A few per cent. soft yellow in gray.
		100	8	Texture like that of 6 : 1 below at 100°.
	6 : 1	300	5	Soft yellow in gray.
		200	5	About 15 per cent. soft yellow in gray.
		150	1	Orange containing fine gray lamellæ or coarse soft yellow lamellæ, or soft yellow lamellæ bordered by gray.
		100	8	
B. Natural bornite containing about 2 per cent. of fine grains of chalcocite				
	5 : 1 *ca.*	300	5 days	The chalcocite gone; 8 to 12 per cent. of angular masses of soft yellow.
		200	5 days	The chalcocite present; traces of soft yellow.
		100	8 days	No change.
C. Synthetic Cu_8FeS_6—300° and 200° for 5 days, 100° for 8 days, 87° for 15 days caused no change.				
D. Chalcopyrite solid solutions				
Sulphur variable	2.4 : 1 to 1.1 : 1			(See text, and Tables 4 to 10, 16 to 18, 21, 24 to 28.)
Sulphur on line between $CuFeS_2$ and $CuFe_2S_3$	1 : 1.2 to 1 : 2			(See text, and Table 21.)
	1 : 1.2	400	1	No notable change.
	1 : 1⅛	400	1	Lamellar structure.
	1 : 1⅜	400	1	Lamellar structure, less distinct than above.
.5 sulphur below $CuFeS_2$ and $CuFe_2S_3$	1 : 1⅛	400	1	Lamellar structure, less distinct than 1 : 1⅛ above.
E. Pyrrhotite solid solutions				(See text.)

[a] See discussion of table.

Table 46.—Until compositions of phases are known more accurately, only tentative explanations of the observations are possible. Thus, the gray constituent may be a chalcocite solid solution ranging from ∝ : 1 to 9 : 1 with iron decreasing with temperature, accompanied by the appearance of (1) a chalcopyrite solid solution, near the 1 : 1 ratio; or (2) bornite if unmixing occurs below about 200°. Quick cooling from higher temperatures of 7 : 1 to 4 : 1 gives an apparently homogeneous orange-colored chalcocite solid solution.

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